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POLARIZATION CHARACTERISTICS OF HIGH-PURITY
IRON-RICH IRON-CHROMIUM-NICKEL ALLOYS
IN SULFURIC ACID SOLUTIONS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By


* * * * * *

The Ohio State University
1966

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I  INTRODUCTION

The electrode kinetic theory is an important and integral part of corrosion and electrochemistry. This theory is founded on certain thermodynamic laws which govern the behavior of metals in aqueous environments. Unlike many chemical and metallurgical investigations, it provides a unique approach to the study of dynamic and rate-controlling electron-transfer reactions.

The processes of corrosion are based on the complex interaction of a few fundamental principles which govern the behavior of materials in aqueous environments. A large segment of research is devoted to the study of these phenomena and is of interest to people involved in manufacturing, construction, and corrosion protection. Results obtained have led to the evaluation and development of materials and methods used in these and in related areas.

Polarization studies have received increasing attention since the investigation by Tafel on hydrogen overvoltage at the beginning of this century. During recent years numerous investigations have been conducted on the polarization behavior of iron, chromium, and nickel in a variety of environments, particularly in sulfuric acid solutions. Many
of these studies are directed toward obtaining a better understanding of the active and passive characteristics of these materials. A review of the literature on the anodic behavior of iron and nickel in sulfuric acid solutions was presented by Economy in 1960. Myers, in 1964, thoroughly discussed the anodic behavior of nickel and chromium in similar environments. Less data, however, are available on the electrochemical properties of binary and ternary alloys of iron, nickel, and chromium. Some of the more pertinent work is reviewed in Part V of this dissertation.

The present investigation was undertaken to study the effect of alterations in alloy compositions on electrode behavior. It is particularly concerned with the anodic and cathodic polarization behavior of iron-chromium-nickel alloys. The latter data are especially needed to understand the complex mechanisms of corrosion and to develop economical materials of industrial importance for systems employing anodic protection as a means of corrosion control. The investigation and the work done herein are part of a program sponsored by the Atomic Energy Commission to establish details of a mechanism for the stress corrosion cracking of iron-chromium-nickel alloys in aqueous environments.

The electrochemical behavior of ten high-purity iron-rich iron-chromium-nickel alloys in hydrogen-saturated 1N H₂SO₄ at 25°C is described. Cathodic and anodic
polarization curves were determined, showing the effect of scan rate, temperature, and solution pH. Particular attention was focused on determinations of corrosion potential, critical current density, passive current density, and Flade relations for pure iron-chromium-nickel. Comparisons with commercially available grades of stainless steel were made whenever possible. The method of investigating these alloys has been the determination of the potential-current characteristics in sulfuric acid.

Current and potential measurements were plotted automatically with a high-speed potentiometric recorder. A unique arrangement of electrical relays coupled to the potential controller provided a wide choice of potential dynamic measurements. The significant characteristic of the experimental apparatus was its ability to record current over 6 orders of magnitude. Current resolution was 0.1 microampere and potential could be read to within 1 millivolt if necessary.

Composition, microstructure, and prior activation treatments were found to have significant effects on polarization characteristics.

Reaction mechanisms are in many cases deduced from electrochemical determinations. The principles of electrode kinetics are used to clarify the polarization curve theory and its application to the study of corrosion mechanisms.
The commercial applications of iron, chromium, nickel, and their alloys, including the extensively used austenitic stainless steels, stimulated much of the interest in this investigation. The complex nature of their active and passive reactions was also an incentive to their study.

The results of this investigation are summarized in Part II of this dissertation. A review of electrode kinetic theory is presented in Part III, a description of the experimental procedure and apparatus is presented in Part IV, and a discussion of the results, including a comprehensive review of the factors which control the anodic behavior of iron-chromium, and nickel and their alloys in sulfuric acid, is given in Part V. Suggestions for future studies are discussed in Part VI.
II SUMMARY AND CONCLUSIONS

The polarization behavior of annealed iron-chromium-nickel alloys in sulfuric acid was investigated by potentiostatic techniques. Ten high-purity iron-rich iron-chromium-nickel alloys containing up to 20 per cent chromium and 20 per cent nickel were chosen to represent one segment of the iron-chromium-nickel ternary diagram. Also included were ten fourth-component Fe-20Cr-15Ni base-alloys and a number of commercial grades of stainless steel. The latter group, of general industrial usefulness, was employed to facilitate interpretation of experimental results. Fourth-component alloying additions were made at one location in the ternary diagram. To provide the most useful information on the effect of alloying, only those elements which exhibit appreciable solid solubility in iron-chromium-nickel alloys were used. The electrolyte was hydrogen-saturated sulfuric acid. Four concentrations (1.0, 0.1, 0.01, 0.001N) were utilized to vary the pH from 0.90 to 3.03.

A discussion of the polarization curve theory is presented in an attempt to clarify its application to the study of corrosion problems. The fundamental principles which govern electrode behavior in aqueous media are described with particular reference to the thermodynamics of
 reversible processes, irreversible polarization characteristics, and environmental control. The determination of anodic and cathodic polarization curves and their use for the evaluation of corrosion properties of metals and alloys are summarized.

The shape of a polarization curve obtained in a potentiostatic experiment depends on the nature of the electrode material, on the characteristics of the solution, and on the method of investigation. A detailed study of the experimental program resulted in the development of a potentiodynamic method which led to entirely satisfactory solutions of the problems considered.

Current and potential measurements were plotted automatically with a high-speed potentiometric recorder. A unique arrangement of electrical relays, coupled to the potential controller, provided a wide choice of potentiodynamic measurements. The significant characteristic of the experimental apparatus was its ability to record current over six orders of magnitude. Current resolution was 0.1 microampere, and potentials, if necessary, could be read to within 1 millivolt.

Since this study is concerned primarily with the influence of alloying elements on the corrosion behavior of metals, the greatest importance of the technique does not lie in the final determination of the rates of corrosion,
but rather in the rapid comparison of fundamental corrosion properties. This is particularly important in the evaluation of a series of experimental alloys.

The anodic polarization behavior of all experimental alloys was determined in dilute sulfuric acid solutions. Sufficient time at open circuit was allotted for each alloy to attain near steady-state conditions before the potential was altered. Current response was recorded automatically as the potential was changed linearly, at a predetermined scan rate, from the open-circuit potential to a potential beyond which oxygen evolution appeared. The current density was calculated on the basis of geometric area from the current-potential curves at 20 millivolt intervals and the data transferred to semilogarithmic paper. Reproducibility was good and the majority of the polarization measurements were determined only once. The experimental results adequately show the effect of composition on the anodic polarization behavior in the chosen environments.

Changes in open circuit potential, critical current density, passive current density, and transpassive behavior are discussed in detail.

1. The pH dependence of the open-circuit potential of pure iron, pure chromium, and pure nickel was determined in dilute solutions of sulfuric acid. Values of 0.06043 volts, 0.06851 volts, and 0.04888 volts, respectively, were found
to agree favorably with the theoretical value of 0.04915 volts for the reversible hydrogen electrode in the same environment.

2. The anodic polarization curves of iron indicate that the critical current density for passivation and the potential at the current maximum are nearly independent of hydrogen ion concentration. Similarly, no correlation between pH and the magnitude of the passive current density is observed, at least in dilute solutions of sulfuric acid.

3. Unlike iron, the hydrogen ion concentration is the deciding factor for the onset of passivation of chromium. The critical current density increases with increasing acidity of the electrolyte.

4. The data indicate that the stability of the passive film on nickel decreases when the concentration of sulfuric acid is raised. Passivation sets in much sooner in solutions of low acidity.

5. The single phase alloys, chromium displaces the open-circuit potential in the negative direction and increases the corrosion current of iron-rich iron-chromium alloys in sulfuric acid. The behavior of chromium in two-phase alloys is more complicated; however, the results are predicted in the theory of mixed potentials.

The beneficial effects of chromium on the corrosion resistance of iron is inherent in its more active electro-
chemical nature. It was observed that chromium favors the onset of passivation by reducing the critical current density and by displacing the passivation potential of iron-chromium and iron-nickel alloys in the negative direction. In addition, chromium lowers the corrosion current in the passive state. This effect is lessened, however, when the nickel content is raised since nickel tends to lower the stability of the passive film in dilute solutions of sulfuric acid. Chromium additions of 10 and 20 per cent to pure iron also shift the transpassive potential of iron-chromium alloys in the negative direction and increase the rate of corrosion in the transpassive region considerably.

The addition of nickel to iron and to iron-chromium alloys displaces the open-circuit potential to more noble values and simultaneously reduces the magnitude of the corrosion current by increasing the overvoltage of the anodic reaction. An increase in the nickel content of iron-nickel alloys results in a slight decrease in the critical current density for passivation and a shift in the potential of the current maximum in the positive direction. A similar response is observed for iron-chromium alloyed with nickel.

Nickel has little effect on the transpassive potential of iron-chromium alloys but it does increase the corrosion rate slightly at high potentials. When nickel alone is added to iron, secondary passivity does not appear until the nickel
content exceeds 10 per cent of the total composition. At higher nickel contents the corrosion current is increased in both the transpassive and secondary passivity regions.

7. Phosphorous, oxygen, silicon, sulfur, and nitrogen in small quantities do not alter the corrosion potential of an Fe-20Cr-15Ni base-alloy. Additions of platinum, carbon, copper, molybdenum, and manganese, on the other hand, induce passivity under the given environmental conditions. Phosphorous is the only element which displaces the active region of the polarization curve in the positive direction. The critical current density is highest in alloys containing silicon, sulfur, and nitrogen and lowest in alloys containing phosphorous and oxygen.

Phosphorous, oxygen, silicon, copper, molybdenum, sulfur, and nitrogen decrease the magnitude of the passive current density of Fe-200Cr-15Ni base-alloys in dilute solutions of sulfuric acid at 25°C. Manganese has little effect on the magnitude of the corrosion current in the passive range, whereas additions of platinum and carbon apparently decrease the stability of the passive film.

All fourth-component additions displace the transpassive potential of the base-alloy in the positive direction. However, little effect, if any, on the magnitude of the corrosion current in either the transpassive or secondary passivity regions is detected. Of all the elements
under investigation only carbon and manganese produce a
noticeable deflection in the polarization curve at poten-
tials beyond the transpassive potential.

8. The shape of the polarization curve depends to
some extent on the rate of change of the electrode potential
because electrode reactions take a finite time to establish
steady-state conditions. Tests in which the traverse rate
of potential is changed from 28.10 to 84.40 to 251.64 milli-
vols per minute reveal that current response varies over an
order of magnitude. All parts of the polarization curve are
equally effected. It may be concluded that the appropriate
selection of the scanning rate must therefore be determined
by the nature of the experimental program and the character-
istics of the system studied. However, once a choice is
made, it would be best to use it for the remainder of the
investigation.

9. Equally important is the temperature at which the
experiment is conducted. Results are given which show that
the general shape of the curve remains constant, however
the rate of dissolution increases significantly with temper-
ature. Since overvoltage is due to a slow stage in the
dissolution process, it is evident that an increase in
temperature decreases overvoltage and stimulates the anodic
reaction.
10. Mounted specimens employed in this investigation were ground to a 600-grit finish through a series of metallographic papers prior to the beginning of each experiment. In lieu of the above, both cathodic and chemical activation treatments were tried; however, the latter proved more successful in rendering the surface of all experimental materials active. Prolonged cathodic pre-treatments passivated the iron-chromium-nickel alloys. The chemical activation treatment consisted of a 5 minute immersion in boiling 1N H₂SO₄.

11. The metallurgical condition of the specimen can have considerable influence on its polarization behavior since dissolution kinetics are dependent upon composition and microstructure. In an attempt to clarify the effect of microstructure on the polarization behavior of stainless steel, two special alloys, similar in composition were prepared. One was ferritic and the other was austenitic. The results illustrate similarities in anodic behavior of the samples. It is apparent that composition, rather than structure, is the predominant factor controlling the dissolution characteristics of iron-chromium-nickel alloys in dilute solutions of sulfuric acid.

12. The above principle was applied to detect the presence of carbide precipitation at grain boundaries of a sensitized Type 204 stainless steel. An additional peak
in the polarization curve of the sensitized specimen, in comparison to the polarization curve of the same specimen in the annealed condition, is attributed to a decrease in chromium content in the grain boundary areas.
III SURVEY OF LITERATURE

A. Equilibration laws of electrochemical reactions

In any electrochemical reaction which occurs between a metal surface and an electrolytic solution there exists a well-defined value for the electrode voltage of the surface. This value designates the thermodynamic equilibrium state of the reaction (1)* An expression for the equilibrium potential can be derived from a statement of the first and second laws of thermodynamics in terms of a change in free energy of the spontaneous electron-transfer reaction. This expression is

$$\Delta F = -w$$  \hspace{1cm} (1)

where $w$ refers to the work done by the system at constant temperature and pressure. For the present only the electrical work which is accomplished during the transport of an electrical charge through a potential gradient will be considered. Drawing from the principles of elementary electrical theory it is shown that

$$\Delta F = -nFE$$  \hspace{1cm} (2)

where $n$ is the number of gram electrons involved in the

---

*Numbers appearing in parentheses refer to the literature cited in the appended bibliography.
reaction and $F$ is the charge of one gram electron. Use of this relationship, however, is rendered cumbersome because of the inherent difficulty in defining the exact cell reaction. A more convenient expression which relates the concentration, or more precisely, the activity of the reacting species to the electromotive force of an electron-transfer reaction is desirable. In its more general form an electrochemical reaction which involves the transfer of $n$ gram electrons can be written as

$$aA + bB + \ldots = 1L + mM + \ldots \quad (3)$$

in which the free energy change in terms of the partial moral free energy is

$$\Delta F = lF_L + mF_M + \ldots - aF_A - bF_B - \quad (4)$$

For the special case when all products and reactants are in their standard states the equation becomes

$$\Delta F^0 = lF_L^0 + mF_M^0 + \ldots - aF_A^0 - bF_B^0 - \ldots \quad (5)$$

Upon subtracting equation (4) from equation (5) it follows that

$$\Delta F^0 - \Delta F = l(F_L^0 - F_L) + m(F_M^0 - F_M) + \ldots$$

$$- a(F_A^0 - F_A) - b(F_B^0 - F_B) - \ldots \quad (6)$$

From the definition of activity $RT\ln A_i = F_i - F^0$ and by the transposition of equation (6) the following expression for the nonequilibrium reaction may be written
\[ \Delta F = \Delta F^0 + RT \ln \frac{a_L^{aM}}{a_A^{a} a_B^{b}} \ldots \]  

Combining equations (4) and (7) yields

\[ E = -\frac{\Delta F^0}{nF} - \frac{RT}{nF} \ln \frac{a_L^{aM}}{a_A^{a} a_B^{b}} \ldots \]  

It is also customary to define \( E_0 \) as the electromotive force of the corresponding cell reaction in which all the reactants and products are in their standard states.

\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_L^{aM}}{a_A^{a} a_B^{b}} \ldots \]  

This equation can be simplified for the case of an electrochemical reaction which occurs between a metal surface and an electrolytic solution containing hydrated ions of the metal in question. The electron-transfer reaction is written

\[ \text{Red} = \text{Ox} + ne^- \]  

where Red and Ox represent the reduced and oxidized form of the metal respectively, for a reaction which involves the transfer of \( n \) gram electrons. Equation (9) becomes

\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}} \]  

The metal to be studied is immersed in a solution which contains its own ions at a known concentration. The potential, \( E \), of the resulting electrochemical cell is measured with respect to a suitable reference electrode. With this information the standard electrode potential, \( E^0 \), may be calculated. For example, the reaction
\[ \text{Fe} = \text{Fe}^{++} + 2e^- \]  

(12)

provided there is unit activity of iron ions in solution, has a reversible potential of \( E^o = -0.44 \) volts. If the potential of the electrode is less (more negative) than -0.44 volts the reduction reaction will be favored, and conversely, if the potential is greater (more positive) than -0.44 volts, the oxidation process will take place. As a general rule the oxidation and reduction processes occur simultaneously. This is necessarily true because if one reaction occurs at a faster rate than the other, a partial separation of charges will be attained. For example, if the rate of ionization exceeds the rate of discharge a difference of potential is established at the metal-electrolyte interface. The potential of the metal becomes negative with respect to the solution. The resultant potential gradient facilitates the discharge process and retards the ionization process. Eventually, equilibration of the forward and reverse reactions occurs and the measured potential is indicative of the thermodynamic equilibrium state of the system.

The standard electrode potentials of most metals when placed in solutions containing their own ions form the basis of the electromotive series. Noble metals which have relatively little tendency to pass into solution as ions, such
as platinum and gold, have high potentials. Base metals which ionize readily, such as sodium and potassium, acquire low potentials.

An important and fundamental principle of electrochemistry can be extracted from the preceding discussion. It states that the direction in which an electron-transfer reaction proceeds on a metal surface depends simply on values related to the electrode voltage, $E$, of the surface and to the equilibrium voltage, $E^0$, of the reaction. According to Faraday's law, this principle can be expressed by relating the rate of an electrochemical reaction to the intensity of the electrical current. Thus

$$ (E-E^0) \times i \geq 0 $$

where the sign of the reactive current, $i$, is considered positive in the case of oxidation and negative in the case of reduction (1).

At present no method is available for the experimental determination of the potential of a single electrode, only the emf of a cell, made by combining two or more electrodes, can actually be measured. However, by choosing an arbitrary zero of potential, it is possible to express the potentials of individual electrodes on an appropriate reference scale. The zero of potential in thermodynamic studies is the potential of a reversible hydrogen gas electrode at one atmospheric pressure in a solution containing hydrogen ions
at unit activity. This electrode, designated 
\[ H_2 (1 \text{ atm})/H^+(a_{H^+} = 1) \] 
is the standard hydrogen electrode and by convention is equal to zero at all temperatures.

The means commonly used to measure electrode potentials is to employ a precision potentiometer. In principle, the potentiometer is an apparatus for accurately measuring the ratio of two voltages. Since one voltage represents the standard cell the other unknown voltage can be determined. The reversible cell is placed so that its emf is in opposition to that of the potentiometer. When the instrument is balanced there is no current passing in either direction and the voltmeter reading represents the emf of the cell.

For example, to determine the potential of the half-cell \( \text{Fe}/\text{FeSO}_4 \) of known concentration, on the hydrogen scale it is joined through a suitable bridge to the normal hydrogen electrode.

\[
\text{Fe}/\text{FeSO}_4 \quad \text{Conductivity} / \quad 1.2 \text{N HCl} / \quad \text{Bridge} / \quad \text{Sat'd with H}_2 / \quad \text{Pt}
\]

The emf of the cell is measured by balancing it on the potentiometer. It would be necessary, however, to compensate for the liquid junction potential introduced by the conductivity bridge. In practice it is more convenient and accurate to employ another reference half-cell such as the Calomel or Silver/Silver Chloride electrode in place of the overly sensitive hydrogen electrode. The potentials of these electrodes are accurately known relative to the normal
hydrogen electrode and their behavior under adverse conditions is more predictable.

B. Mechanics of electrochemistry

Electrochemical reactions require the presence of an anode and a cathode. By definition the terms anode and cathode denote surfaces at which the positive current enters and leaves the cell, respectively. The study of corrosion is concerned with reactions which occur between a metal and its environment. The basic nature of corrosion is almost always the same, that is, a flow of electricity is established between an anode and cathode when exposed to an electrolytic environment capable of transporting electrically charged ions. An electrolyte is any liquid containing cations (atoms or a grouping of atoms carrying a net positive charge) and anions (atoms or a grouping of atoms carrying a net negative charge). The anode and cathode may be two different metals or merely different areas on the same piece of metal. The electrochemical theory considers that both anodic and cathodic areas may exist simultaneously on a metal surface as discrete particles (2). The distribution of these particles fluctuates with time, producing what appears to be uniform corrosion attack, in spite of the fact that metal dissolution occurs only at anodic sites. In all cases a potential difference must exist between the two
areas to insure a flow of current. Current flow and consequently the corrosion rate must increase with an increase in the potential gradient. All that remains to complete the circuit is a metallic conducting path through which negatively charged particles may travel. The expression relating the flow of current in coulombs and the amount of metal dissolved at the anode is effectively stated in the Laws of Michael Faraday (3):

The amount of chemical decomposition produced by a current is proportional to the quantity of electricity passing through the electrolytic solution.

The amounts of different substances liberated by the same quantity of electricity are proportional to their chemical equivalent weights.

Generally, any metal may serve as anode or as cathode in an electrochemical cell depending on the characteristics of the metal with which it is coupled. It is also possible to make a certain metal behave anodically or cathodically with respect to a suitable inert electrode by applying a corresponding positive or negative potential to the resulting cell.

In acid solutions the cathodic reaction may involve the discharge of hydrogen ions on discrete areas of the metal surface. The release of hydrogen ions results in the accumulation of a relatively high concentration of hydroxyl ions which increase the alkalinity of the electrolyte immediately adjacent to the cathode. In neutral or in slightly alkaline solutions the evolution of hydrogen gas is
very slow and the accumulation of a layer of hydrogen on the metal surface stifles the electron-transfer reaction by a process called cathodic polarization (4). An increase in the oxygen content accelerates corrosion by reacting with the hydrogen to form water, thereby depolarizing the cathode. Other cathodic reactions which may compete in corrosion processes are:

\[ 4H^+ + O_2 + 4e^- = 2H_2O, \]
\[ O_2 + 2H_2O + 2e^- = H_2O_2 + 20H^- \text{, and} \]
\[ O_2 + 2H_2O + 4e^- = 40H^- \]

The importance of understanding the mechanics of electrochemistry cannot be overemphasized. At present there is a large discrepancy in the assigned convention used by numerous people in this field. Based on the work of A. J. deBethune (5), a brief introduction to the subject is presented to clarify the conventions used in this report.

### 1. Whole-cell reactions

When combining two electrodes to form a whole cell a diagram is drawn which implies that the cell reaction takes place when positive electricity in the form of cations flows through the cell from left to right when the cell is short-circuited. Under these conditions the electromotive force is positive as in the cell

\[ \text{Pt, } H_2(g), \text{ HCl (a=1), Cl}_2(g), \text{ Pt} \]

(15)
for which the cell reaction is

\[ H_2 + Cl_2 = 2H^+ + 2Cl^- \]  

(16)

By letting the symbols \( V' \) and \( V'' \) denote "the electrical potentials in pieces of the same kind of metal connected with the anode and cathode respectively"(6) then the electromotive force \( E^o \) is equal to \( V''-V' \) as in

\[ (V''-V')^o = V^o(Pt,Cl_2,Cl^-)-V^o(Pt,H_2,H^+) = E^o + 1.359V \]  

(17)

By convention, the electromotive force—"is equal in sign and magnitude to the electrical potential of the metallic conducting lead on the right when that of a similar lead on the left is taken as zero, the cell being open" (7).

In the above example the hydrogen electrode on the left is the anode and negative terminal

\[ H_2 = 2H^+ + 2e^- \]  

(18)

The chlorine electrode on the right is the cathode and the positive terminal

\[ Cl_2 + 2e^- = 2Cl^- \]  

(19)

Reversing the direction of current flow inverts the cell diagram and changes the sign of the electromotive force from positive to negative in the following manner;

\[ Pt, Cl_2(g), HCl (a=1), H_2(g), Pt \]  

(20)

in which

\[ 2H^+ + 2Cl^- = H_2 + Cl_2 \]  

(21)
consequently,

\[(V''-V')^0 = V^0(Pt,H_2,H^+) - V^0(Pt,Cl_2,Cl^-) = E^0 = -1.359V \] (22)

The inversion of the cell diagram is a matter of convention only, whereas the change in the sign of the electromotive force is a requirement of the second law of thermodynamics. By definition the first cell reaction produces electromotive energy and is called a galvanic cell. The second cell reaction can occur only through the input of electromotive energy from an external source and is called an electrolytic cell.

In summary, cations always flow from left to right, that is, from the anode to the cathode in a conventional cell diagram thereby changing the polarity of the electrode on the left from negative, as in a galvanic cell, to positive, as in an electrolytic cell. In the above example, the chlorine electrode is always the positive terminal and the hydrogen electrode is always the negative terminal.

2. **Half-cell reactions**

In electrochemistry an important and often used connotation is the half-cell reaction (8). An example is the Cl\(^-\), Cl\(_2\), pt electrode which when coupled to the normal hydrogen electrode on the left

\[Pt, H_2, H^+ \parallel Cl^-, Cl_2, Pt \] (23)
implies the reaction
\[ \frac{1}{2} H_2 + \frac{1}{2} Cl_2 = H^+ + Cl^- \] (24)
The electromotive force of this reaction is called the electrode potential of the chlorine electrode because by definition
\[ E^0(Pt, H_2, H^+) = E^0(H^+, H_2, Pt) = 0 \] (25)
On the other hand, when the half-cell Pt, Cl_2, Cl^- is coupled to the normal hydrogen electrode on the right
\[ Pt, Cl_2, Cl^- || H^+, H_2, Pt \] (26)
the following reaction is implied
\[ Cl^- + H^+ = \frac{1}{2} Cl_2 + \frac{1}{2} H_2 \] (27)
By convention, the electromotive force of this reaction is not referred to as the electrode potential.

If these principles are applied to the whole-cell reaction previously discussed it may be concluded that the half-cell emf of the standard chlorine electrode has two values equal in magnitude but opposite in sign, thus
\[ 2e^- + Cl_2 = 2Cl^- \ldots E^0(Cl^-, Cl_2, Pt) = +1.359 \] (28)
\[ 2Cl^- = Cl_2 + 2e^- \ldots E^0(Pt, Cl_2, Cl^-) = -1.359 \] (29)
The sign of the electromotive force of a half-cell reaction, therefore, depends on the direction of current flow. It is a property of the reaction which occurs at the electrode surface and not of the electrode.
Although it is a fact that the electromotive force \( E^0 = V'' - V' \) of the standard hydrogen-chlorine cell changes its sign when the current flow is reversed, the same is not true of the potential difference between the standard chlorine and standard hydrogen electrodes. In the latter case the potential difference remains sign-invariant when the direction of current flow is reserved.

\[
V^0(\text{Pt, Cl}_2, \text{Cl}^-) - V^0(\text{Pt, H}_2, \text{H}^+) = +1.359V
\]  

(30)

A moment's reflection indicates that the electrode potential on the standard chlorine electrode is

\[
V^0(\text{Pt, Cl}_2, \text{Cl}^-) = V^0(\text{Cl}^-, \text{Cl}_2, \text{Pt}) = +1.359V
\]  

(31)

In comparison the following values are indicated (9):

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Half-reaction</th>
<th>( E^0 )</th>
<th>( V^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Cl}^-, \text{Cl}_2, \text{Pt}</td>
<td>\text{2e}^-+\text{Cl}_2=\text{2Cl}^-</td>
<td>+1.359</td>
<td>+1.359</td>
</tr>
<tr>
<td>\text{Pt,Cl}_2, \text{Cl}^-</td>
<td>\text{2Cl}^-=\text{Cl}_2+\text{2e}^-</td>
<td>-1.359</td>
<td>+1.359</td>
</tr>
</tbody>
</table>

(32)

Studies by deBethune (5) show "this tabulation emphasizes once again the fact that the half-cell emf, as a measure of the electromotive work available in a given half-reaction changes its sign when the half-reaction is reversed; the electrode potential, as a property of the electrode at which the two half-reactions are in equilibrium, remains sign-invariant."

This is consistent with thermodynamic principles. The increase in free energy for a reversible cell at constant
temperature and pressure is

\[ \Delta F = nFE \quad (33) \]

Taking as an example the standard chlorine-standard hydrogen electrode in which

\[ V^0 = V_{Cl}^0 - V_{H^+}^0 = -V_{Cl}^0 \quad (34) \]

the spontaneous reduction reaction is written

\[ \Delta V = -2F(-V_{Cl}^0) = -2FV_{Cl}^0 \quad (35) \]

Similarly for the oxidation or reverse reaction it follows that

\[ \Delta V = 2F(V_{Cl}^0) = 2FV_{Cl}^0 \quad (36) \]

which demonstrates that the sign of the free energy is changed when the reaction is reversed as required by the second law of thermodynamics.

The advantages of using the "electrode potential" as based on the thermodynamics of J. Willard Gibbs are two-fold:

1. The sign is independent of the direction of current flow, and
2. The method is consistent with laboratory observations.

It is far more elegant and useful than the terms "oxidation potential" and "reduction potential" which differ in sign and context (10).
C. Electrode kinetic theory

Thus far the discussion has been concerned primarily with equilibrium electron-transfer reactions based on valid thermodynamic principles. The laws formulated serve as a foundation for modern electrochemical theory. Corrosion processes, however, are seldom restricted to ideal reversible electrode behavior. Deviation from equilibrium conditions is the rule rather than the exception. A more workable solution is required by engineers to combat the destructive forces of corrosion. This solution is made available in the study of irreversible electrode behavior. The following discussion of electrode kinetics is conducive to the development of modern methods of corrosion control.

A departure of the electrode potential from its reversible value is called polarization. Polarization or over-voltage, $\eta$, is defined as the change in potential of an electrode which results from current flow to or from the surface. This is shown in the following expression

$$\eta = E_i - E_r$$  \hspace{1cm} (37)

where $E_i$ is the electrode potential when a net current flows and $E_r$ is the reversible electrode potential. To appreciate the significance of this relationship and the term over-voltage, it is necessary to deviate from reversible behavior and to expound on the equation

$$\Delta F = -nFE^0$$  \hspace{1cm} (38)
for nonequilibrium conditions, that is, for the case when a net current flows. For example, the cell

\[ \text{Cu} \ || \ Fe^{++} \ || \ H^+(aH^+ = 1) \ || \ H_2(pH_2=1 \text{ atm}) \ || \ Pt \text{ Cu} \]  

(39)
in which the measured emf is the electrical potential difference between two pieces of the same kind of metal connected with the anode and cathode. For the present it is not necessary to correct for the liquid junction potential represented by the double bars drawn between the two electrodes. If a positive current is made to flow left to right as in an electrolytic cell, the cell reaction is written

\[ \text{Fe} + 2H^+(aH^+ = 1) + 2e^- = \text{Fe}^{++} + H_2(pH_2=1 \text{ atm}) + 2e^- \]  

(40)
The anodic and cathodic reactions are

\[ \text{Fe} = \text{Fe}^{++} + 2e^- \ (a) \]  

(41)
and

\[ 2H^+(aH^+ = 1) + 2e^-(c) = H_2(pH_2 = 1 \text{ atm}) \]  

(42)
respectively. Representing the partial molal free energy or chemical potential of species i by \( \mu_i \) the following equation is applied to the \( \text{Fe} \ || \ \text{Fe}^{++} \) electrode.

\[ \mu \text{Fe} = \mu \text{Fe}^{++} + 2\mu e^- \ (\text{in } \text{Fe}) \]  

(43)
A measure of the escaping tendency of electrons is alternately designated as \( \overline{\mu} \), the electrochemical potential.
The expression for the normal hydrogen electrode is similarly written

$$2\mu H^+(aH^+=1) + 2\mu e^-(in\ Pt) = \mu H_2(pH_2=1\ atm)$$  \hspace{1cm} (44)

By combining equations (43) and (44), as in equation (40), it follows that

$$\mu Fe + 2\mu H^+(aH^+=1) + 2\mu e^-(in\ Fe) = \mu Fe^{++} + \mu H_2(pH_2=1\ atm) + 2\mu e^-(in\ Pt)$$  \hspace{1cm} (45)

After rearranging terms equation (45) becomes

$$2[\mu e^-(in\ Fe) - \mu e^-(in\ Pt)] = \mu Fe^{++} + \mu H_2(pH_2=1\ atm) - \mu Fe - 2\mu H^+(aH^+=1)$$  \hspace{1cm} (46)

The free energy change of the cell reaction is given by the right-hand side of equation (46)

$$\Delta F = \mu Fe^{++} + \mu H_2(pH_2=1\ atm) - \mu Fe - 2\mu H^+(aH^+=1)$$  \hspace{1cm} (47)

which is a measure of the potential difference $E$ of the cell.

$$E = 2[\mu e^-(in\ Fe) - \mu e^-(in\ Pt)]$$  \hspace{1cm} (48)

In general it follows

$$\frac{\Delta F}{nF} = -E = -[\mu e^-(in\ Fe) - \mu e^-(in\ Pt)]$$  \hspace{1cm} (49)

which, for a reversible electrochemical reaction, becomes

$$E + [\mu e^-(in\ Fe) - \mu e^-(in\ Pt)] = 0$$  \hspace{1cm} (50)

Upon inspection it appears that

$$U_{rev} = [\mu e^-(in\ Fe) - \mu e^- (in\ Pt)]$$  \hspace{1cm} (51)
where $U_{rev}$, according to Van Ryssilberghere (7), represents the reversible electrode potential. Therefore,

$$E + U_{rev} = 0$$  \hspace{1cm} (52)

designates electrochemical equilibrium. For nonequilibrium conditions $E + U_{rev}$ is no longer equal to zero but to some quantity called the electrochemical tension, $E$, or, $\eta$, overvoltage

$$\bar{E} = U + E \neq 0$$  \hspace{1cm} (53)

The thermodynamic significance of this is shown by substituting $E$ from equation (52) into equation (53),

$$\bar{E} = U + (-U_{rev})$$

$$E = U - U_{rev}$$  \hspace{1cm} (54)

where $U$ is the irreversible electrode potential and $U_{rev}$ is the reversible electrode potential. When positive current flows through the cell from left to right $E$ is composed of the sum of three positive terms—

1. The ohmic drop in the cell,
2. The anodic overvoltage, and
3. The absolute value of the cathodic overvoltage.

Alternately, when positive electricity flows through the cell from right to left the electrochemical tension is made up of the sum of three negative terms.
The extent of deviation from reversibility depends upon local-action or corrosion currents accompanied by a slow chemical attack which polarize discrete anodic and cathodic areas of the metal surface. In accordance with Faraday's law metal dissolution is occurring only at the anodic sites, however as a requirement of the electrochemical theory of corrosion, the anodic and cathodic reactions are free to fluctuate with time on the surface of the electrode. When current flow is established on the corroding metal the potential of the cathode changes in a negative direction because of polarization effects. The compromise or corrosion potential is equal to the polarized potential achieved by the composite of anodes and cathodes on the metal surface. Also, the intersection of the anodic and cathodic polarization curves represents the maximum value that is attained by the short-circuited cells and, therefore, is called the "maximum corrosion current" (2). The relative position of the resultant corrosion potential and corrosion current is shown in the classical polarization diagram reproduced in Figure 1. For simplicity, \( E_A \) represents the reversible anode potential of the metal and \( E_c \) denotes the reversible cathodic potential, which in the case of electrode reactions involving evolution of hydrogen, is the equilibrium hydrogen electrode potential. Actually, the corrosion current approaches but never reaches its maximum value due to the
Fig. 1. Polarization Diagram for a Corroding Metal.
presence of ohmic drops in the cell. It is evident that factors which influence the corrosion potential, such as (1) the impurity content of the metal, (2) the nature of the anions present, (3) the pH of the solution, and (4) the concentration of dissolved oxygen, alternately affect the corrosion rate of the metal. For example, the presence of dissolved oxygen in electrolytic solutions depolarizes the cathodes and increases the local-action currents, which, in turn, shifts the corrosion potential in the cathodic direction. In electrochemical measurements, therefore, reversibility is better in systems free of depolarizers.

Experimental electrochemical techniques, when used to study polarization behavior of metal systems, make an important contribution to research for they enhance our knowledge of electrochemical phenomena associated with many corrosion processes. Wagner and Traud (11) give a detailed account of uniform corrosion based on the principles of superposition of partial current-potential curves and, also provide experimental proof of the validity of this principle for dissolution of zinc amalgams in acid solution. Mueller (12), Stern (13), and Makrides (14) discuss these relations further and show that they are correct for a number of reactions. A thorough knowledge of the electrode kinetic theory provides the corrosion engineer with a means of explaining many of the experimental observations in the field.
1. Ohmic drop

If the electrolyte in the vicinity of the electrode has an appreciable resistance, the passage of current will give rise to a potential difference which obeys Ohm's law. The magnitude of this potential drop, temporarily excluding the resistance due to oxides or other poorly conducting films, is dependent on the experimental set-up and on the conductivity of the solution. A knowledge of polarization effects associated with IR drops may be obtained by studying the characteristics of electrolytic conductivity.

According to Ohm's law, \( E = IR \), the strength of the current flowing in an electrochemical cell depends on the magnitude of the electromotive force and on the electrical resistance of the electrolyte. It is convenient for this discussion to define a property known as the conductance, \( G \), or conductivity of an electrolytic solution which is equal to the reciprocal of the resistance. In terms of Ohm's law this gives

\[
I = EC
\]  

(55)

An increase in conductivity permits a larger current flow for a given applied emf. In other words, conductivity can be defined as the ability of a solution to conduct an electric current. The conducting power of an electrolyte is determined by the total number of ions present in solution and on the mobility of the ions (3). For example, hydrogen
and hydroxyl ions have the highest mobility, therefore, strong acids and bases are better conductors than solutions of salts. Weak acids and bases are poor conductors because they contain relatively few ions.

It is better, for purposes of comparison, to use specific resistance, which is the resistance of a cube 1 centimeter on a side, or more correctly, specific conductance, \( k \), which is the reciprocal of specific resistance. The actual conductivity of a particular electrolyte in an electrochemical cell which contains electrodes having an exposed area of a square centimeters and placed 1 centimeter apart is equal to

\[
\frac{ka}{l}
\]

(56)

Substituting this term for \( C \) yields

\[
I = \frac{Eka}{l}
\]

(57)

It is apparent for a given emf that the conducting power of an electrolyte can be improved by--

1. Increasing the size of the electrodes, 
2. Bringing the electrodes closer together, and 
3. Adding conducting salts to the solution.

It is imperative in electrolytic polarization studies to find the difference in potential of an electrode at known current densities when a net current flows and when the electrode is at equilibrium. It is, therefore, desirable to
exclude IR drops from polarization measurements. The means generally employed to measure the potential of an electrode in an electrolytic cell is to use a Luggin-Haber capillary, which is connected to an external reference electrode through a tube of electrolyte. The potential of the electrode is measured while current flows through the cell. To minimize the inclusion of an IR drop the top of the Luggin-Haber probe is drawn to a fine point and brought close to the surface of the polarized electrode. When the top of the probe is located in front of but away from the surface of the electrode it does not disturb the equipotential lines. The potential distribution around the electrode is maintained, provided, of course, the current density is uniform (15). When the probe is brought closer to the electrode it cuts the equipotential lines and distorts the potential field causing the current density to become nonuniform. At extremely close distances polarization measurements are too low.

Barnartt (16) concluded from a study on the magnitude of IR-drop corrections in electrode polarization measurements made with a Luggin-Haber probe that a capillary tip of diameter d may be placed as close as 2d from the electrode surface with negligible shielding error. The potential measured from a parallel plane electrodes differs from the actual polarization potential by a factor

$$V_{IR} = \frac{5}{k}$$

(58)
where \( i_0 \) is the current density and \( k \) is the solution conductivity. The term \( \delta \) represents the distance between the desired potential and the potential measured at the tip of the capillary. This distance is shown in the schematic diagram of Figure 2. In the design of practical cells for electrode polarization measurements Barnartt found that Pyrex glass capillaries of outer diameter \( d = 0.02 \) centimeter are convenient to use with a high-impedance potentiometer. The magnitude of IR drops in millivolts for a capillary tip of diameter \( 0.02 \) centimeter situated \( 0.04 \) centimeter from a plane electrode are given in Table 1. An accuracy of \( \pm 1 \) millivolt is possible when the solution conductivity is greater than \( 1(\text{ohm-centimeter})^{-1} \) and the current density less than \( 3 \times 10^{-1} \) ampere-centimeter\(^{-2}\).

In addition, an ohmic drop is induced when the electron-transfer reaction produces a film of appreciable resistance on the surface of the electrode (17). This IR drop is more difficult if not impossible to correct for, although in some cases it is preferable to consider this potential part of the polarization voltage. Under limiting conditions several methods are available which may be used to eliminate all ohmic drops. These experimental procedures are based on the theory that the ohmic potential decays simultaneously when the current to the electrode is shut off. The initial potential-decay curve is recorded when the
Fig. 2. Schematic Diagram of IR Drop in the Electrolyte between Capillary Tip and Electrode. After Barnartt (16).
circuit is open and any IR drop can be spotted and eliminated. These methods are not conducive to an accurate interpretation of ohmic potentials when polarization is large and the current density is high.

TABLE 1. IR Correction in Millivolts for a Capillary Tip of Diameter 0.02 Centimeter Situated 0.04 Centimeter from a Plane Electrode (16)

<table>
<thead>
<tr>
<th>(i_0 (\text{amp. cm}^{-2})/k(\text{ohm cm})^{-1})</th>
<th>1</th>
<th>10^{-1}</th>
<th>10^{-2}</th>
<th>10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3 \times 10^{-1})</td>
<td></td>
<td>10</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>(3 \times 10^{-2})</td>
<td>1</td>
<td>10</td>
<td>100</td>
<td>1,000</td>
</tr>
<tr>
<td>(3 \times 10^{-3})</td>
<td>0.1</td>
<td>1</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>(3 \times 10^{-4})</td>
<td>0.01</td>
<td>0.1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>(3 \times 10^{-5})</td>
<td>0.001</td>
<td>0.01</td>
<td>0.1</td>
<td>1</td>
</tr>
</tbody>
</table>

Note: Values below dashed lines, according to Barnartt, indicate the ranges of \(i_0\) and \(k\) over which polarization measurements are corrected readily with an accuracy of ± 1 millivolt.

2. Concentration polarization

A surface reaction, in general, will induce a change in concentration of the species with which it is associated. The species is replenished or depleted depending on the nature of the reaction. As a result, a concentration gradient is established between the surface at which the reaction occurs and the bulk of the solution. If the concentration of species in the bulk of the solution remains
constant, steady-state conditions are approached. When the reaction considered is electrolytic, these concentration changes affect the electrode potential. For example, if the rate of metal dissolution at the anode is greater than the rate of escape of metal ions from the vicinity of the electrode, the concentration of cations in the solution near the anode becomes greater than in the bulk of the electrolyte. This results in a shift of the anode potential toward more noble values than that observed at equilibrium. The potential shift increases with increasing current density. A similar but opposite effect occurs at the cathode. Eventually, at some sufficiently high current density, called the limiting current density, the concentration gradient in the boundary layer of either electrode approaches a maximum.

Concentration changes which affect the electrode potential are a cause of irreversible electrode behavior. The term concentration overvoltage is used to designate irreversibility of this type.

The processes involved in the movement of ions through a solution are—

1. Migration,
2. Convection, and
3. Diffusion.

Migration is the movement of ions toward the surface under the influence of an electric field. When a supporting
electrolyte is used which does not participate in the reaction, transport of the reacting species by migration is negligibly small. Mass movement of fluids due to mechanical stirring or to density differences between one part of the solution and another is due to convection currents. Movement of ions through a solution by diffusion is the most influential process affecting concentration polarization. The development of a diffusion layer at the electrode/electrolyte interface is an important concept in electrochemistry. This interphase region has properties (chemical, electrical, hydrodynamic) different from those which exist in the bulk of the solution. The following connotation for the interphase region has been adopted by the CITCE Commission on Electrochemical Nomenclature and Definitions and by the IUPAC Sub-commission on Electrochemical Symbols and Terminology (7).

\[ \begin{array}{c|c|c|c|c} 
 I & & & & II \\
 a & b & c & d 
\end{array} \]

Starting from Phase I which is metallic, the remainder of the region is comprised of a transfer layer a-b, a diffuse layer b-c, and in the case of passage of current a diffusion layer c-d. When electrochemical equilibrium is achieved,
the diffuse layer is followed by phase II which represents the bulk of the electrolyte. The properties of the transfer layer are similar to those of an adsorbed layer in which the electrons take part in the electrode reactions. Beside the transfer layer is the diffuse layer which has at every point a non-zero charge density and non-zero gradients of electrical and chemical potentials. These characteristics are present at zero current and at all currents different from zero. The diffusion layer, in the presence of current, differs in composition from the bulk phase. It has an electric charge density which is practically negligible or equal to zero, however, it also has electrical and chemical potential gradients which are appreciably smaller than those in the diffuse layer. In the absence of natural convection currents the surface d is at infinite distance from the metallic phase. When current flows the thickness of the diffusion layer exceeds the thickness of the diffuse layer. Even in the presence of current the transfer layer and the diffuse layer make up what is known as the electrochemical double layer. It consists only of these portions of the interphase region in which the local electrical charges are not equal to zero. Ideally the electrode potential is equal to the potential of the metallic phase minus the potential of the solution at the extreme interface, d, of the diffusion layer. It is the latter potential which is corrected for in polarization measurements.
When ionic diffusion is the rate controlling stage in the dissolution of a corroding metal concentration polarization results. Consequently there will be a concentration gradient in passing from the electrode to the electrolyte. The diffusion layer is illustrated in Figure 3 which shows the variation of concentration with distance from the surface. Since the true concentration profile is cumbersome to handle mathematically, it is assumed that in the steady-state the concentration gradient on a plane surface is linear (3). It is apparent that the rate at which ions diffuse outwardly through the layer is equal to

\[
\frac{AD}{\delta} (C_a - C_b)
\]

(59)

where \(A\) is the exposed area of the electrode surface, \(D\) is the diffusion coefficient of the ions, and \(\delta\) is the thickness of the diffusion layer. The concentration of ions at the surface and in the bulk of the solution is represented by \(C_a\) and \(C_b\) respectively. The cations which are transported away from the electrode by the normal process of migration are also to be considered. If \(t_A\) is the transport number of the ions in the diffusion layer and \(n\) is the valency, then the rate in gram-moles per second at which ions are removed from the surface of an electrode of unit area by migration is

\[
\frac{t_A I}{nF}
\]

(60)
Fig. 3. Concentration Profile in the Vicinity of an Electrode During Electrolysis.
where \( I \) is the current and \( F \) represents the Faraday.

Under steady-state conditions the rate of ionic dissolution is equal to the sum of the rates of diffusion and migration, so that for unit area

\[
\frac{I}{nF} = \frac{D}{\delta} (C_a - C_b) + \frac{T_A}{nF} I
\]

\[
I = \frac{DnF(1-t_A \delta)}{t_0} (C_a - C_b)
\]

where \( t \), written in place of \( 1-t_A \), is equal to the sum of the transference numbers of all other ions in the diffusion layer.

It is obvious that in any given solution the rate of dissolution will approach a maximum value which corresponds to the limiting current \( I_L \).

\[
|I_L| = \frac{DnFCA}{t_0}
\]

(62)

When the current is increased above this value an alternate electrode reaction such as the liberation of oxygen begins. This is usually indicated by a sharp rise in the electrode potential. For the case of anodic dissolution the limiting current is reached when the rate of dissolution exceeds the rate of diffusion, that is, when ions are formed faster than they are dispersed into solution.
The value for the electrode potential when no current is flowing is determined by the concentration of ions in the bulk of the solution. Thus, the equilibrium reversible potential is given by

\[ E_R = E^0 - \frac{RT}{nF} \ln C_b \]  

(63)

If the electrode processes, other than diffusion, are all rapid, then the irreversible electrode potential is found by using the concentration of ions on the surface of the electrode. In the simplest case

\[ E_I = E^0 - \frac{RT}{nF} \ln C_a \]  

(64)

The magnitude of concentration polarization is equal to the difference in the above two expressions, provided activation overvoltage and the potential drop due to the ohmic resistance of the electrolyte is neglected. Thus,

\[ \eta_c = E_I - E_R \]  

(65)

\[ \eta_c = \frac{RT}{nF} \ln \frac{C_b}{C_a} \]

The activities of the species should be used in place of concentrations for greater accuracy.

Replacing the factor \( \frac{DnF}{tD} \) in equation (61) by \( k \) for brevity, it follows that

\[ I = k (C_a - C_b) \]  

(66)
Solving for $C_b$

$$C_b = C_a - \frac{I}{k} \quad (67)$$

Inserting this expression into equation (65) for $C_b$ gives

$$\eta_c = \frac{RT}{nF} \ln \left(1 - \frac{I}{kC_a}\right) \quad (68)$$

also

$$\eta_c = \frac{RT}{nF} \ln \left(1 - \frac{I}{DnF} \frac{1}{5t} C_a\right) \quad (69)$$

It follows from equation (62) that

$$\eta_c = \frac{RT}{nF} \ln \left(\frac{I^0 - I}{I^0}\right) \quad (70)$$

is the form in which the magnitude of the concentration polarization is frequently expressed (18).

3. **Activation polarization**

Surface reactions which have a large energy of activation are slow compared with other processes of anodic dissolution which results in an overpotential of a different type called activation polarization. The evolution of hydrogen and oxygen exhibits overpotentials of this kind.

Previously it was shown that when a metal is immersed in an aqueous solution containing free metal ions there is a tendency for metal atoms to pass into solution and ions from the solution to be discharged onto the metal surface. The
two opposing processes are represented by the reaction

\[
M + n\text{H}_2\text{O} \xrightleftharpoons[k_2]{k_1} M (\text{H}_2)_n^+ + e^-
\]

(71)

If in the absence of a potential difference, the forward reaction is more rapid than the reverse reaction, cations accumulate on the solution side of the electrode and free electrons left on the metal build up what is known as the electrical double layer. The resultant potential across the double layer is the single electrode potential. These occurrences make it more difficult for positive ions to leave the negatively charged electrode but they facilitate the discharge of ions from the solution. At equilibrium the dissolution and discharge processes occur at the same rate and the electrode exhibits its reversible potential.

According to the theory of absolute reaction rates, in the absence of a potential difference, the rate of a reaction is equal to the specific rate multiplied by the activities of the reacting species (19). Under standard state conditions the rates of the two opposing processes are \( k_1 \) and \( a_+ k_2 \) where the activity of the metal is chosen as unity and the activity of the hydrated ions is taken as \( a_+ \).

A simplified potential energy curve for the dissolution of a solid metal is illustrated in Figure 4. The potential energy at A is that of an atom of the metal and the potential
Fig. 4. Potential Energy Barrier at an Electrode Surface.
energy at C is that of an ion in solution. At equilibrium
the reversible potential, E, of the electrode will act
between A and C, i.e., across the energy barrier. It is
evident that a fraction, $\alpha$, of this potential will facili-
tate the dissolution process while the remainder, $1 - \alpha$,
hinders the reverse or discharge process. The free energy
of the metal atom which passes into solution is increased,
during its transfer across the double layer, by the factor
$\alpha n FE'$; where n is the valence of the ion and F is the
Faraday. Hence, the specific rate of the forward reaction
becomes

$$ k_1' = k_1 e^{\frac{\alpha n FE'}{RT}} \tag{72} $$

Similarly, the specific rate of the reverse reaction, i.e.,
the conversion of ions into atoms, becomes

$$ k_2' = a_+ k_2 e^{-\frac{(1 - \alpha)n FE'}{RT}} \tag{73} $$

At equilibrium the two rates are equal and the poten-
tial $E'$ may be replaced by the equilibrium reversible
potential $E$, thus

$$ k_1 e^{\frac{\alpha n FE}{RT}} = a_+ k_2 e^{-\frac{(1 - \alpha)n FE}{RT}} \tag{74} $$

By rearranging terms equation (74) is

$$ e^{\frac{\Delta \text{FE}^0}{RT}} = a_+ e^{-\frac{n FE}{RT}} \tag{75} $$
where $\Delta F^0$ is equivalent to the standard free energy of the over-all direct process, i.e., the transfer of atoms on the electrode to ions in solution. It follows that

$$E = -\frac{\Delta F^0}{nF} - \frac{RT}{nF} \ln a_+ \quad (76)$$

Equation the quantity $-\frac{\Delta F^0}{nF}$ to the standard electrode potential $E^0$, results in the familiar Nernst equation for the potential of a reversible electrode.

$$E = E^0 - \frac{RT}{nF} \ln a_+ \quad (77)$$

The above observation applies to the case when the net current flow is zero. The potential is changed, however, when the electrode is made an anode or cathode so that the rate of one of the processes exceed that of the other. For example, at an anode the rate of the ionization process is greater than that of the discharge process. The magnitude of the current flowing is determined by the difference in the two rates. The amount of charge transferred during an electrochemical reaction is equal to the product of the Faraday, $F$, the charge of one gram-electron (96,500 coulombs) and the number, $n$, of gram-electrons transferred through the external circuit when the reaction occurs to the extent of the number of gram-moles represented by the cell reaction. Thus, the anodic current per unit area is given by the equation
\begin{align*}
I_a &= nFk_1 e^{\frac{\alpha nFE}{RT}} \\
I_c &= nFk_2 e^{-\left(1-\alpha\right)nFE} \\
\text{and the cathodic current per unit area by the equation} \\
I_c &= nFk_2 e^{-\left(1-\alpha\right)nFE} \\
\text{where } a \text{ is written in place of } a^+ \text{ for the activity of the} \\
\text{cations in the immediate vicinity of the electrode and } E' \\
\text{is used in place of } E \text{ to indicate that it differs from the} \\
\text{reversible potential for the given electrode. By definition,} \\
\text{this difference is equal to } \eta_a, \text{ the activation overpotential.} \\
\text{Substituting } E + \eta_a \text{ for } E' \text{ in equations (78) and (79) the} \\
\text{expressions for the anodic and cathodic current can alternatively be written} \\
I_a &= nFk_1 e^{\frac{\alpha nF(E+\eta_a)}{RT}} \\
I_c &= nFk_2 e^{-\left(1-\alpha\right)nF(E+\eta_a)} \\
\text{respectively. Since the current corresponding to the} \\
\text{electrode reaction is the algebraic sum of the anodic and} \\
\text{cathodic components which cross the transfer layer simultaneously in opposite directions, the net current flow,} \\
\text{assumed to be anodic becomes} \\
I &= I_a - I_c \\
I &= nFk_1 e^{\frac{\alpha nF}{RT}} \left[ e^{\frac{\alpha nF\eta_a}{RT}} - e^{\frac{(1-\alpha)nF\eta_a}{RT}} \right] \\
\end{align*}
Equation (82) is known as the Tafel equation for anodic dissolution. At electrochemical equilibrium the anodic and cathodic components of the reaction current in the transfer layer are equal in absolute value. The common absolute value of the two components is called the transfer exchange current, or the exchange current, which is designated $I_o$. Thus, at equilibrium $I_a = I_c = I_0$, where $I_0$ from equation (82) is equal to

$$I_0 = nFk_l e^{\frac{\eta F E}{RT}} \quad (83)$$

The final expression for the net current flow of a metal immersed in an aqueous solution which contains free metal ions is

$$I = I_0 \left[ e^{\frac{\eta F n_a}{RT}} - e^{-\left(1-\eta\right)\frac{nF n_a}{RT}} \right] \quad (84)$$

For small values of $\eta_a$, i.e., when the net current flow is very low, equation (84) can be expanded and simplified to give

$$I = I_0 \left( \frac{nF n_a}{RT} \right) \quad (85)$$

or, by rearranging terms

$$\eta_a = \frac{RTI}{nF I_0} \quad (86)$$

Since the actual potential of the electrode is related to $\eta_a$ it follows that when some stage in the dissolution process is rate-determining the anode potential is a linear
function of the current at low values of polarization. On the other hand, when \( \eta_a \) is very large, the terms in the expansion of the exponentials in equation (84) cannot be neglected. However, it is possible to simplify the expression since the second term decreases rapidly as \( \eta_a \) increases and thus becomes insignificant in comparison to the first term which increases as \( \eta_a \) increases. At large currents, then equation (84) reduces to

\[
I = I_0 e^{\frac{nF \eta_a}{RT}} \quad (87)
\]

or

\[
\eta_a = -\frac{RT}{\alpha nF} \ln I_0 + \frac{RT \ln I}{nF} \quad (88)
\]

This equation is usually expressed in the following form

\[
\eta_a = a + b \log I \quad (89)
\]

where \( a \) and \( b \) are constants. It is evident that the overvoltage and the anode potential are in a linear function of the logarithm of the current density when the current flow is high.

In the preceding derivation no consideration was given to the effect of a change in concentration of metal ions in the electrolyte. Such a change is obvious when the current flowing to or from the electrode is large as in equation (89). Here, it was assumed that the concentration of metal ions at the surface of the electrode is equal to
the concentration of metal ions in the bulk of the solution. This is an ideal condition that is never attained in electrochemical studies. The following derivation is more appropriate for this discussion of anodic polarization since it considers the combined effects of activation and concentration polarization on the magnitude of the irreversible electrode potential. Since there is a net flow of ions due to anodic dissolution the concentration or activity of cations in this region is dependent upon the rate at which ions leave the surface of the electrode. At equilibrium the rate of dissolution is equal to the rate of diffusion, therefore equation (82) (using $E'$ instead of $E$ and $\eta_a$) can be related to equation (61)

$$nF[k_1 e \frac{\alpha FE'}{RT} - k_2 a e \frac{(1-\alpha)FE'}{RT}] = \frac{DnF}{t_b} (a-a_b)$$

$$a = k_1 e \frac{\alpha FE'}{RT} + \frac{D_{ab}}{t_b} \frac{D}{t_b + k_2 e \frac{(1-\alpha)FE'}{RT}}$$

If this value for $a$ is inserted into equation (82) the result is

$$I = nF \left[ \frac{k_1}{k_2} e \frac{\alpha FE'}{RT} - a_b \right] \frac{1}{\left[ \frac{1}{k_2} e \frac{(1-\alpha)FE'}{RT} + \frac{t_b}{D} \right]}$$

(91)
According to equation (75), \( \frac{k_1}{k_2} \) is equal to \( e^{(+\Delta F^0/RT)} \) and since by equations (76) and (77), \( \Delta F^0 \) is equivalent to \(-nFE^0\), where \( E^0 \) is the standard potential of the electrode, it follows that

\[
I = nF \frac{\frac{nF(E' - E^0)}{RT} - ab}{\frac{1}{k_2} e^{\frac{(1-\xi)nFE'}{RT}} + \frac{t\delta}{D}}
\]  

(92)

This expression represents the variation of the electrode potential \( E' \), with the current \( I \), when the net flow of current is in the anodic direction. As equation (91) is somewhat complicated, it may be simplified in two limiting cases. First, if \( k_2 \) is small, so that the discharge of ions is the rate-determining state, the term \( t\delta/D \) in the denominator of equation (92) can be neglected and the latter becomes equal to

\[
I = nF \left[ k_1 e^{\frac{\xi nFE'}{RT}} - k_2 a_b e^{\frac{-(1-\xi)nFE'}{RT}} \right]
\]  

(93)

which is identical to equation (82) except that \( a_b \), the activity of the ions in the bulk of the solution replaces \( a \), the activity of the ions on the surface of the electrode. This condition is applicable only when the current is very low.

The other limiting case, which is most frequently encountered, arises when diffusion is the rate-determining
stage. Under these circumstances, $k_2$ is large and the first term in the denominator of equation (92) can be neglected, hence

$$I = \frac{nFD}{t_0} \left[ e^{\frac{nF(E^\prime - E^\circ)}{RT}} - a_b \right]$$

(94)

4. Acid corrosion

A modification of equation (94) can be applied to a metal dissolving in an acid solution which contains little or none of the ions of the metal. Under these conditions $a_b$ is set equal to zero and since most of the current is transported by hydrogen ions this is practically unity so that equation (94) reduces to

$$I = \frac{nFD}{t_0} e^{\frac{nF(E^\prime - E^\circ)}{RT}}$$

(95)

The magnitude of the current is equivalent to the quantity of metal dissolved in the acid. To find the cathodic reaction consideration must be given to the theory of hydrogen overvoltage (19).

The reaction commonly used to express the discharge of hydrogen ions on the surface of an electrode immersed in an aqueous solution is

$$H_3O^+ + e^- \xrightleftharpoons{k_1}{k_2} \frac{1}{2} H_2(gas)$$

(96)
According to a previous definition the specific rate of the discharge of an ion under the influence of an electrode potential \( E' \) is equal to

\[
k_1 = k_1 A_+ e^{-\frac{\alpha F E'}{RT}}
\]

(97)

where \( E' \) is the total potential operative between the solution and the cathode. It appears that the overvoltage is dependent upon the hydrogen ion concentration at a constant current density, however it was shown that at low current densities the overvoltage is independent of the pH of the electrolyte, provided the concentration of extraneous ions is negligible. In order to satisfy the experimental requirements the specific rate equation is written

\[
k_1 = k_1 a_+ e^{\frac{(1-\alpha)F \eta_a}{RT}}
\]

(98)

where \( \eta_a \) is the overvoltage portion only of the total cathode potential. This is explained by theorizing that the total electrode potential \( E' \) is operative across two double layers. The reversible hydrogen potential operates across the outer "solution double layer" whereas the overvoltage portion is only effective over the inner "electrode double layer." At equilibrium the electrode potential is equal to that of the reversible hydrogen electrode, consequently the potential of the "electrode double layer" is zero. When a net current flows the electrochemical
equilibrium of the innermost layer is disturbed and a difference of potential, equal to the overvoltage, is set-up. If the potential energy barrier for the passage of ions across the inner layer is the higher of the two then equilibrium is not disturbed in the "solution double layer." It follows that the specific rate of discharge of hydrogen ions is given by equation (98) and similarly the specific rate of the reverse reaction is

$$k_2 = k_2 e^{\frac{(1-\alpha)nF\eta_a}{RT}}$$

(99)

Proceeding as before, the rates of the forward \((v_1)\) and reverse \((v_2)\) reactions, in units (atoms, molecules or ions) per square centimeter, is written

$$v_1 = a_1 k_1 e^{-\alpha F\eta_a \over RT}$$

(100)

and

$$v_2 = a_2 k_2 e^{(1-\alpha)nF\eta_a \over RT}$$

(101)

respectively. At the reversible potential \(a_1 k_1 = a_2 k_2\) the magnitude of the net current passing is given by the difference between these two rates,

$$I = nF[a_1 k_1 e^{-\alpha F\eta_a \over RT} - a_2 k_2 e^{(1-\alpha)nF\eta_a \over RT}]$$

(102)

where each reacting unit is regarded as carrying the equivalent of a single charge. Again two limiting cases are apparent. First, if the overvoltage is very low the expon-
entials may be expanded and all non-linear terms neglected, thus

\[ I = nF \left( a_1 k_1 \left[ 1 - \frac{\alpha F \eta_a}{RT} \right] = a_2 k_a \left[ 1 + \frac{(1 - \alpha) F \eta_a}{RT} \right] \right) \tag{103} \]

Assuming that \( a_1 k_1 = a_2 k_2 \) for small values of \( \eta_a \) equation (103) becomes

\[ I = \frac{nF a_1 k_1 F \eta_a}{RT} \tag{104} \]

Second, when the overvoltage is high the rate of the discharge reaction greatly exceeds the rate of the reverse reaction and the result is

\[ I = nF a_1 k_1 e^{-\frac{\alpha F \eta_a}{RT}} \tag{105} \]

This relationship is true for many cathodes from which hydrogen is discharged. The most commonly reported value for \( \alpha \) is 0.5 which indicates that the energy barrier of the "electrode double layer" is almost symmetrical.

Corrosion of most metals immersed in an acid solution containing relatively few cations of the metal is a diffusion controlled process. The magnitude of the anodic current for n-valent ions is given by equation (95). When there is no actual flow of current the anodic current \( I_a \), is exactly balanced by the cathodic current \( I_c \), which results from the discharge of hydrogen ions. Disregarding the current due to the passage of hydrogen gas into solution as ions, the
cathodic current given by equation (105), is written in the form

$$I_c = nF\alpha_{H_2O}k_1 e^{-\frac{\alpha FE}{RT}}$$  \hspace{1cm} (106)$$

where $\alpha_1$ is replaced by $\alpha_{H_2O}$, the activity of the water at the surface of the electrode. By definition, activation overpotential $\eta_a$, is equal to the potential $E'$ of the electrode when a net current flows minus the equilibrium reversible potential $E$, i.e., the potential of the hydrogen electrode in the same solution. The latter potential is equal to $-\frac{RT}{F} \ln a_{H_3O^+}$ on the assumption that the standard potential of hydrogen is zero. It follows from equation (106) that

$$I_c = nF\alpha_{H_2O}k_1 a_{H_3O^+} e^{-\frac{\alpha FE'}{RT}}$$  \hspace{1cm} (107)$$

When equilibrium is achieved the values of $I_a$ and $I_c$, as given by equations (95) and (107) respectively, must be equal, hence,

$$\frac{nF}{Q} e^{\frac{nF(E'-E^o)}{RT}} = nF\alpha_{H_2O}k_1 a_{H_3O^+} e^{-\frac{\alpha FE'}{RT}}$$  \hspace{1cm} (108)$$

Solving this equation for $E'$, it is found that

$$E' = \frac{nE^o}{n+x} + \frac{RT}{(n+x)F} [Q + \ln a_{H_2O} - \ln a_{H_3O^+}]$$  \hspace{1cm} (109)$$

where $Q$ is a constant for the given metal equal to $\ln \frac{5k_1}{D}$. 
Since \( a_{H_2O} \) may be taken as unity, it follows that

\[
E' = C - \frac{RT}{(n+\alpha)F} \ln a_{H_3O^+}
\]

(110)

where \( C \) is a constant. The electrode potential is therefore a linear function of the pH of the solution. For a bivalent metal \( n \) is 2 and since \( \alpha \) is generally taken to be 0.5, the slope of the straight line should be approximately 0.012 volts at ordinary temperatures. Experimentally, this is true in solutions of high acidity. In solutions of low acidity, however, the term \( \alpha \ln a_{H_3O^+} \) is negligible in comparison with \( Q + \ln a_{H_2O} \) and the potential is independent of pH.

5. **Polarization characteristics**

In electrochemical studies it is often desirable to distinguish and to identify the forms of polarization which manifest themselves in irreversible electrode behavior. Generally this is accomplished by associating observed experimental behavior with the characteristics of the three types of overpotential determined from the general theory developed in this discussion. Some of the differences are enumerated below.

Agitation of the electrolyte by stirring has a pronounced effect on the magnitude of the limiting current density. Concentration polarization falls when the limiting current density is increased by stirring. On the other hand,
the degree of agitation has little or no effect on activation overpotential or on ohmic drops in the electrolyte (18).

Activation polarization is strongly influenced by the nature and physical state of the electrode, whereas concentration overpotential is not unless surface irregularities protrude beyond the diffusion layer.

Similarly, a distinction can be made between activation overpotential and ohmic drops in the electrolyte by observing the rate of potential decay when the current flow to or from the electrode is abruptly stopped. Resistance overpotential decays instantaneously, whereas activation overpotential decreases at a rapid but measurable rate when the circuit is broken.

The effect of temperature on polarization is shown by a simple differentiation of equation (82) which relates temperature, current, and concentration overpotential.

\[
\left( \frac{\partial \eta_c}{\partial T} \right)_I = \frac{\eta_c}{T} - \frac{RT}{F} \frac{I}{(I-I_O)} \left( \frac{\partial \ln I_O}{\partial T} \right) \tag{111}
\]

If I is much greater than \(-I_O\) equation (111) reduces to

\[
\left( \frac{\partial \eta_c}{\partial T} \right)_I = \frac{\eta_c}{T} - \frac{RT}{F} \left( \frac{\partial \ln I_O}{\partial T} \right) \tag{112}
\]

When the temperature is raised the diffusion coefficient increases and the thickness of the diffusion layer decreases, hence, the second term on the right hand side of Equation (112) is always positive and equal to 0.04 per degree in
most cases. The magnitude of the temperature coefficient is found by taking \( \eta_c = 0.150 \) volts and \( T = 300^\circ K \) so that

\[
\left( \frac{\partial \eta_c}{\partial T} \right)_I = -0.0005 \text{ volts/degree}
\]  

(113)

Agar and Bowden (18) observed that under similar conditions the temperature coefficient of activation overpotential is considerably higher, about \(-0.0025 \) volts per degree. Resistance overpotential decreases at a much slower rate.

D. Mixed potential theory

To illustrate the principles discussed it is convenient to resort to a graphical representation which shows the relationship between overvoltage and current for the anodic \((I_a)\) and cathodic \((I_c)\) reactions of a simple electrode system (20). An example would be a metal M immersed in a solution containing its ions M\(^+\) in which the reaction rate and current flow are directly related according to Faraday's law. The relationship between the oxidation and reduction rates and the exchange current, \(I_c\), at the equilibrium potential, and the effect of polarization on these rates, is shown in Figure 5. When the reaction rates are controlled by a slow step requiring an activation energy the dependence of current on overvoltage is given by equation (88). Thus, for the anodic reaction

\[
\eta_a = 2.3 \frac{RT}{\Delta F} \log \frac{I_a}{I_o}
\]  

(114)
and similarly for the cathodic reaction

\[ \eta_a = 2.3RT \log \left( \frac{I_c}{I_0} \right) \]  \hspace{1cm} (115)

where current flow is considered positive in both the anodic and cathodic directions. When electrode equilibrium is disturbed by external forces the reaction rates vary as shown in Figure 5. Experimentally the external polarization current, \( I_E \), is not a measure of the individual reaction rates but is a measure of the difference between the two rates. For example, when the electrode is polarized anodically the net current flow is given by the relation \( I_{EA} = I_A - I_C \), where \( I_{EA} \) is the external anodic current when the electrode is polarized to some overvoltage value, \( \eta_a \). At a sufficiently large overvoltage, i.e., when the potential of the electrode is much greater than the reversible potential, \( I_{EA} \) approaches \( I_A \). Similarly, if the electrode is polarized cathodically the external current is given by the relation \( I_{EC} = I_C - I_A \).

The only values which can be measured experimentally are \( I_{EA}, I_{EC}, \) and \( \eta_a \). According to the theory of activation polarization a linear (Tafel) relationship exists between \( \eta_a \) and \( \log I_A \) or \( \log I_C \), however only the experimental values \( \eta_a \) and \( \log I_{EA} \) can be measured and plotted. The theoretical relationship between activation overvoltage and the logarithm of the external anodic current is found by substituting \( I_{EA} + I_C \) into equation (114).
Fig. 5. Relationship between Overvoltage and Current for the Anodic and Cathodic Reactions of a Single Electrode System. After Stern and Geary (20).
Knowing the relation between $\eta_a$ and $I_c$ from equation (115) a curve can be constructed showing the variation of $\eta_a$ with $\log I_{EA}$ as illustrated in Figure 6. The diagram indicates that the Tafel slope deviates from linearity at low applied currents where the magnitude of the cathodic current is still sufficiently large to influence the shape of the curve. Stern and Geary (20) suggest that experimental verification of the linear relationship between $\eta_a$ and $\log I_{EA}$ requires that current measurements be made over a range of approximately two logarithmic cycles of current. Estimates of the Tafel constants require measurements in the region of 1000 times $I_0$. The magnitude of the exchange current is found by extrapolating the Tafel region to the reversible potential.

Another factor which must be considered in electrochemical studies is the notable effects caused by a change in ionic concentration in the electrolyte. Accurate measurements of activation and concentration overpotential are not possible unless the characteristics and limitations of both are thoroughly understood. The relationship between concentration polarization and current is given by equation (82) which in its simplest form is

$$\eta_a = 2.3 \frac{RT}{\alpha F} \log \frac{I_{EA} + I_c}{I_o}$$  \hspace{1cm} (116)
Fig. 6. Relationship between Overvoltage and Applied Anodic Current for a Single Electrode System. After Stern and Geary (20).
where $I_L$, the limiting diffusion current for anodic dissolution is equal to

$$I_L = \frac{DnFa}{t^6}$$

The terms used in both equations have their usual significance. Concentration polarization becomes effective when $I_A$ approaches $0.1 I_L$ as shown in Figure 7. Note that the shape of the curve beyond the Tafel region deviates from linearity at high current values as a result of concentration polarization.

Still another phenomenon which interferes with the measurements of activation overpotential is the existence of ohmic potential drops in the electrolyte. However, since the resistance term $I_{EAR}$ is a linear function of current, a significant deviation occurs only at high current values. The effect of resistance polarization on the relationship between overvoltage and applied anodic current for a single electrode system is shown in Figure 8.

Polarization diagrams which represent the corrosion of a metal in an aggressive environment are more complex than those for a noncorroding electrode system. For example, a metal immersed in an acid solution usually subsists two co-existing oxidation-reduction systems. One electrochemical reaction involves the dissolution and discharge of metal ions.
Fig. 7. Effect of Concentration Polarization on the Relationship between Overvoltage and Applied Anodic Current for a Single Electrode System. After Stern and Geary (20).
Fig. 3. Effect of Resistance Polarization on the Relationship between Overvoltage and Applied Anodic Current for a Single Electrode System. After Stern and Geary (20).
\[ M + nH_2O \rightleftharpoons M(H_2O)^{n+} + e^- \]  

(119)

while the second electron-transfer reaction

\[ 2H_3O^+ + 2e^- \rightleftharpoons H_2(gas) \]  

(120)

is inherent in the oxidizing or reducing capabilities of the electrolyte. Both reactions exhibit an exchange current and Tafel slope characteristic of the electrochemical system (20). The steady-state potential of the corroding metal occurs when the total rate of oxidation equals the total rate of reduction. Hence, at equilibrium

\[ I_{AM} + I_{AH} = I_{CM} + I_{CH} \]  

(121)

where \( I_{AM} \) is the rate of oxidation of the metal and \( I_{CM} \) is the rate of reduction of metal ions. \( I_{AH} \) and \( I_{CM} \) represent the rates of oxidation and reduction of the environment, respectively. At the corrosion potential, according to Faraday's law, the total rate of dissolution of the metal is equal to \( I_{AM} - I_{CM} \) or, conversely, by \( I_{CH} - I_{AH} \). When an external current is applied in the anodic direction \( I_{CM} \) and \( I_{AH} \) become insignificant in comparison to \( I_{CH} \) and \( I_{AM} \). In other words, when the potential of the electrode is sufficiently removed from the equilibrium potential the corrosion rate is given by \( I_{CH} \) or \( I_{AM} \). The relationship between overvoltage and current for a corroding electrode system which consists of two co-existing electrochemical
reactions is illustrated in Figure 9. Equations which represent the reaction rates are—

**Metal Oxidation**

\[ \eta_a = E_M^o + \beta_M \log \frac{I_{AM}}{I_{o,M}} \quad (122) \]

**Metal Reduction**

\[ \eta_a = E_M^o - \beta_M \log \frac{I_{AH}}{I_{o,M}} \quad (123) \]

**Hydrogen Oxidation**

\[ \eta_a = E_H^o + \beta_H \log \frac{I_{AH}}{I_{o,H}} \quad (124) \]

**Hydrogen Reduction**

\[ \eta_a = E_H^o - \beta_H \log \frac{I_{CH}}{I_{o,H}} \quad (125) \]

The value of the equilibrium potential of the opposing electron-transfer reactions is approximately equal to the potential at which \( I_{AM} = I_{CH} \). An imaginary line drawn from the intersection of these two reaction rates and projected to the abscissa gives the corrosion current of the given electrode system.

An expression which describes the shape of the experimental anodic polarization curve of a corroding electrode is derived in the following manner. The external applied anodic current, \( I_{EA} \), is equal to the difference between the sum of the rates of all the reduction reactions, thus

\[ I_{EA} = (I_{AH} + I_{AM}) - (I_{CH} + I_{CM}) \quad (126) \]
Fig. 9. Relationship between Overvoltage and Current for a Corroding Electrode System Consisting of Two Coexisting Electrochemical Reactions. After Stern and Geary (20).
By definition the local action current, under steady-state conditions, is given by the relation

$$I_{LA} = I_{CH} - I_{AH}$$  \hspace{1cm} (127)$$

which when substituted into equation (126) gives

$$I_{EA} = I_{AM} - I_{CM} - I_{LA}$$  \hspace{1cm} (128)$$

but

$$\eta_a = E^0_M + \beta_M \log \frac{I_{AM}}{I_{O,M}}$$  \hspace{1cm} (129)$$

therefore,

$$\eta_a = E^0_M + \beta_M \log \frac{I_{EA} + I_{CM} + I_{LA}}{I_{O,M}}$$  \hspace{1cm} (130)$$

Since the variations of $I_{CM}$ and $I_{LA}$ with $\eta_a$ are known (equations 123, 124, and 125) the overpotential as a function of applied anodic current can be calculated from equation (130). The expected curve is shown in Figure 10.

It is evident that true Tafel behavior for a corroding electrode is delayed to much higher values of applied current by comparison with Figure 6 for a noncorroding electrode system. Also, the Tafel region is shortened when concentration polarization and ohmic drops in the electrolyte are considered. In this case equation (130) becomes

$$\eta = E^0_M + \beta_M \log \frac{I_{EA} + I_{CM} + I_{LA}}{I_{O,M}} + 2.3 \frac{RT}{nF} \log \frac{I_L - I_{EA} - I_{LA}}{I_L} - I_{EAR}$$  \hspace{1cm} (131)$$
Fig. 10. Relationship between Overvoltage and Applied Anodic Current for a Corroding Electrode System. After Stern and Geary (20).
The combined polarization effects on the relationship between overvoltage and applied anodic current for a corroding electrode system are illustrated in Figure 11.

It can be concluded that deviations from Tafel behavior is caused by local action currents, concentration polarization, and ohmic potential drops in the electrolyte.

E. Laboratory techniques

The most common electrochemical method for studying corrosion reactions is the measurement of the net current flow as a function of potential. If the principles of electrode behavior are closely observed then it does not matter whether the potential is controlled and the current measured or whether the current is controlled and the potential measured. Frequently the characteristics of the system will dictate the most logical choice to be used.

Before applying such data to any corrosion problem the environment in which the metal is placed must be considered. Since most problems deal with aqueous solutions it is imperative to become familiar with the characteristics and limitations of these environments. Water has two very important roles in electrochemical studies (21).

First, at low electrode potentials hydrogen is liberated and at high potentials oxygen is liberated due to the decomposition of water. This immediately sets limits to the
Fig. 11. Effect of Concentration Polarization and Resistance on the Relationship between Overvoltage and Applied Anodic Current for a Corroding Electrode System. After Stern and Geary (20).
potential range over which the behavior of a metal and its ions can be studied. Second, aqueous environments provide a ready source of hydroxyl ions which aid in the formation of hydroxides and oxides of the metal if such products are thermodynamically stable.

Galvanostatic or constant current experiments are used most frequently in the laboratory because the circuitry is much simpler than that required to achieve constant potential conditions. The current, derived from a battery in series with a variable resistance, is passed between the working electrode and a counter electrode as illustrated in Figure 12. Here the circuit is such as to provide a current which will remain constant regardless of what may happen within the cell. It is essential that the external resistance be much greater than the internal resistance of the cell. The current may be measured with a sensitive ammeter or indirectly by determining the potential across a standard resistor. In both galvanostatic and potentiostatic experiments the potential of the working electrode is measured with respect to a standard reference electrode such as the calomel, hydrogen, or silver-silver chloride electrode. An instrument with high input impedance and a null detector are used to keep the current flow between the working and reference electrode at a minimum. If appreciable current is drawn, the reference electrode may become polarized and
Fig. 12. *Galvanostatic Circuit for Determining Polarization Curves.*
the current density on the working electrode may change in an unknown way.

The electrical connections to all electrodes must be isolated from the test solution to avoid contamination and spurious current density readings (22). Metals such as platinum and tungsten when used as electrical leads can be fused in glass to provide liquid-tight seals. Other materials such as lacquers, waxes, and thermosetting plastics contaminate the solution. A suitable electrode assembly has been described by Stern and Makrides (23) which utilizes Teflon and glass. This demountable electrode assembly is not objectionable because the materials used in its construction are inert to many of the common test solutions.

Electrode preparation is governed by the nature of the material and of the environment being investigated. For instance, the surface of the metal may be abraded on metallographic paper or electropolished. To remove organic impurities the electrodes are cleaned in a mixture of sulfuric and chromic acids or in boiling concentrated nitric acid. In addition, a suitable solvent may be used to remove distorted metal from the surface of the electrode, or the material may be deeply etched to achieve a constant surface area to volume ratio. The latter is most critical in the initial stages of anodic dissolution. Frequently, it is desirable to use a solvent which is similar to the
test solution in order to accelerate the attainment of steady-state conditions. Generally the last step is to flush the electrode copiously with conductivity water before placing it into the cell. Since impurities have a tendency to attach themselves to the surface of clean electrodes, measurements should be made soon after the electrodes are immersed into the test solution.

The electrochemical cell should be constructed solely of pyrex glass and Teflon. The latter is used to eliminate the need for silicon grease around stopcocks and other entries to the cell. Provisions should be made for a controllable atmosphere. This is done most effectively by using fritted glass disks to disperse the gas evenly through the test solution and by installing water traps at gas exits. If tests are conducted for a long period of time the anode and cathode should be installed in individual compartments separated by a coarse fritted disk. It should also be possible to pre-electrolyze the solution either before or after the cell is filled. If done after, two identical auxiliary electrodes, one in each compartment, are required. The cell must be so constructed that a uniform current distribution on the working electrode is maintained at all times. Depending on the requirements of the experiment, provisions for additional components, such as for temperature control, for agitation of the solution, and for pH measurements may be required.
The purity of the solution must also be considered. Obviously more precautions are necessary for studies of reaction mechanisms than for corrosion tests conducted in solutions obtained from industrial installations where the effect of purity is the factor to be investigated. In the laboratory, however, trace impurities may have a profound and undesirable affect on electrochemical measurements. Here, solutions may be made from recrystallized reagents and conductivity water in which the last distillation treatment is performed over alkaline potassium permanganate to remove organic impurities (24). The reaction vessel and all glass components are cleaned in a saturated solution of potassium dichromate in concentrated sulfuric acid (Cleaning Solution). After the cell is filled it is preferable to pre-electrolyze the solution at a potential exceeding the maximum operating potential of the experiment. This prevents the occurrence of secondary reactions from interfacing with true electrode behavior.

1. Reference electrodes

The potential of the corroding electrode is measured against a suitable reference electrode. Two of the most widely used reference electrodes for electrode kinetic measurements are the saturated calomel electrode and the platinized platinum hydrogen electrode. Silver/silver-
chloride and glass electrodes, because of their limited applicability, are used less frequently in polarization work.

**Calomel electrode**

The mechanics of the calomel electrode are found in many tests on electrochemistry, notably among them are *Introduction to Electrochemistry* by Samuel Glasstone (3) and *Electrochemistry, Principles and Applications* by E. C. Potter (25). In essence, two equilibria are satisfied in the calomel half-cell. First, mercurous chloride is soluble to a small extent and is in equilibrium with its ions in the electrolyte

$$\text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{Hg}_2^{++} + 2\text{Cl}^-$$ \hspace{1cm} (132)

Second, mercury metal is in equilibrium with mercurous ions.

$$\text{Hg}_2^{++} + 2\text{e}^- \rightleftharpoons 2\text{Hg}$$ \hspace{1cm} (133)

The over-all reaction, by combining equations (132) and (133) is

$$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$$ \hspace{1cm} (134)

Since mercurous chloride and mercury are both conventionally at unit activity in the calomel half-cell the application of

$$E = E^o - \frac{RT}{nF} \ln \frac{\text{Product of activity of resultants}}{\text{Product of activities of reactants}}$$ \hspace{1cm} (135)
to the equilibrium reaction, yields

\[ E_{\text{calomel}} = E^0 - \frac{2.303 \cdot RT}{F} \log a_{\text{Cl}^-} \]  

(136)

The value of \( E^0 \) at 25°C for the calomel half-cell is +0.2677 volts, therefore

\[ E_{\text{calomel}} = 0.2677 - 0.0591 \log a_{\text{Cl}^-} \]  

(137)

When the chloride activity appropriate to each potassium chloride solution is substituted into equation (137) the potential of the calomel electrode is found. For example, the potential of the Hg/Hg2Cl2 saturated potassium chloride electrode is

\[ E_{\text{calomel}} = 0.2420 \text{ volts} \]  

(138)

According to Potter (25), the potential of the above calomel half-cell decreases with increasing temperature. The temperature coefficient applicable at ambient temperatures is -0.65 millivolt per degree centigrade. Although discrepancies between different sets of measurements exist, the approximate potential of the calomel half-cell is 0.2257 volts at 50°C and 0.2095 volts at 75°C.

Commercially available calomel electrodes are acceptable for polarization work (14). Electrical contact with the electrolyte is maintained by a liquid junction through a fiber sealed in the tip of the electrode. The loss of
potassium chloride to the electrolyte is negligible, nevertheless its concentration should be maintained at full saturation at all times.

**Hydrogen gas electrode**

The hydrogen gas electrode at one atmosphere pressure is the standard to which all other electrodes are referred. It consists of a small platinum sheet or wire coated with finely divided platinum black. Platinization is carried out by electrolysis of a solution of chloroplatinic acid containing a small amount of lead acetate (26). The platinized platinum electrode is partially immersed in the experimental solution through which a stream of extremely pure hydrogen is passed at atmospheric pressure. According to Glasstone (3), this arrangement permits the rapid attainment of equilibrium between the electrode material, the hydrogen gas, and the solution. It is imperative to remove oxygen, dust, and other impurities from the hydrogen gas since they may influence the functioning of the hydrogen electrode (24). Gas bubbled through alkaline permanganate and alkaline pyrogallol solutions or diffused through a palladium or palladium-silver tube heated at 325°C is sufficient.

Hydrogen gas which is adsorbed by the finely divided platinum black is quick to establish an equilibrium between
molecular hydrogen, hydrogen ions in solution, and electrons, thus

\[ H_2(\text{gas}) \rightleftharpoons H_2(\text{Pt}) + 2H_2O \rightleftharpoons 2H_3O^+ + 2e^- \]  

Equilibrium is rapidly attained in either direction, therefore the electrode behaves as one which is reversible with respect to hydrogen ions. The electrode potential of the reversible hydrogen electrode under any given conditions of hydrogen gas pressure in atmospheres and hydrogen ion concentration in gram-ions per liter is

\[ E_H = E^o - \frac{RT}{nF} \ln \left( \frac{a_{H_3O^+}}{a_{H_2}} \right) \]  

When the activities of the hydrogen ion and the hydrogen gas are both unity then \( E_H = E^o \). By convention, \( E_H = 0 \) so that \( E^o = 0 \). Hence, by referring to the normal reversible hydrogen electrode as zero, the above equation becomes

\[ E_H = - \frac{2.303 \, RT}{nF} \log \left( \frac{a_{H_3O^+}}{a_{H_2}} \right) \]  

or, at \( 250^\circ C \)

\[ E_H = -0.05915 \log a_{H_3O^+} + 0.030 \log a_{H_2O} \]  

When the activity of hydrogen gas is unity, i.e., at one standard atmosphere of pressure, equation (142) reduces to

\[ E_H = -0.05915 \log a_{H_3O^+} \]
By definition, $\text{pH} = -\log a_{\text{H}_3\text{O}^+}$, so that

$$E_H = +0.05915 \ \text{pH}$$

(144)

**pH measurements**

According to the Stockholm convention (7)

if a cell is formed by combining any half-cell $X$ with the standard hydrogen half-cell (SHE), the measured potential of the electrode in question relative to that of the standard hydrogen electrode taken as zero is called the electrode potential of $X$. Thus, if the electrode $X$ is positive with respect to the SHE, the electrode potential of $X$ is positive. The sign of the electrode potential is the experimentally measured sign of the cell emf if the SHE is on the left and the electrode in question on the right.

For example, the emf of the cell

$$\text{Pt} | H_2(1 \ \text{atm}) | H_3O^+ (a=1) \parallel X^+ | X$$

(145)

is, by convention

$$E = E_X|X^+ - E^{0}_{\text{H}_2} | H_3O^+ = E_X|X^+$$

(146)

The most frequent use of the type of half-cell described above is for the determination of hydrogen ion concentration or activity in a given solution. For pH measurements the hydrogen half-cell is connected electrically to another reference half-cell, preferably to the calomel electrode, by means of a suitable conductivity bridge. The potential, $E$, of such a cell is measured with a potentiometer.
or other circuitry of high input impedance. No appreciable current flow must result from this determination.

Consider the following cell which consists of a hydrogen electrode immersed in a solution of sulfuric acid and a saturated calomel electrode

\[
\text{Pt}(H_2) \bigg| H_2SO_4(m) \bigg| Hg_2Cl_2 \bigg| Cl^-
\]

(147)

The electrode reactions are as before

\[
H_2(g) \leftrightarrow 2H_3O^+ + 2e^-
\]

(148)

and

\[
Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^-
\]

(149)

thus, the overall reaction is

\[
Hg_2Cl_2 + H_2 \leftrightarrow 2H_3O^+ + 2Hg + 2Cl^-
\]

(150)

According to equation (135) the emf of the cell becomes

\[
E = E^0 - \frac{RT}{nF} \ln \left( \frac{(a_{H_3O^+})^2 (a_{Hg})^2 (a_{Cl^-})^2}{(a_{Hg_2Cl_2}) (a_{H_2})} \right)
\]

(151)

Since the mercurous chloride and mercury are both conventionally at unit activity in the calomel half-cell and choosing the hydrogen pressure so that \(a_{H_2} = 1\) ideal gas, \(P = 1\) atmosphere, equation (151) reduces to

\[
E = E^0 - \frac{RT}{nF} \ln (a_{H_3O^+})^2(a_{Cl^-})^2
\]

(152)
By rearranging terms and substituting the appropriate values equation (152) reduces to

\[ E = E^0 - 0.05915 \log a_{H^3O^+} - 0.05915 \log a_{Cl^-} \]  

(153)
at 25°C.

However, from equations (137) and (143), it is possible to write

\[ E = E_{calomel} + 0.05915 \text{pH} \]  

(154)

where \( E_{calomel} \) refers to the potential of the saturated calomel half-cell at 25°C. The pH of the given solution is found from the expression

\[ \text{pH} = \frac{E - E_{calomel}}{0.05915} \]  

(155)

which relates the hydrogen ion concentration (activity) to the difference in the experimentally measured potential of the cell and the potential of the saturated calomel reference electrode. In the above derivation the liquid junction potential is considered negligible.

In precise work, the potential, \( E \), of such a cell is corrected to the value \( E' \) which it would have if the partial pressure of hydrogen were one atmosphere by means of the equation

\[ E' = E + \frac{RT}{nF} \log \rho \]  

(156)
The partial pressure, $p$, in atmospheres, is obtained by subtracting the vapor pressure of the solution in the vessel from the observed barometric pressure. The values of pH may then be computed from the corrected potential, $E'$, and equation (155). MacInnes (27) regards this as the standard procedure for determining pH values. The accuracy of other methods is judged by the exactness with which they conform to it.

2. Description of a polarization diagram

The anodic polarization behavior of most metals follows the relationships previously developed in the discussion of electrode kinetic theory over a limited range of potentials. In galvanostatic experiments the potential increases almost linearly with the logarithm of the applied current up to a certain critical current density, $i_c$. At currents larger than that corresponding to $E$ a transition to another reaction, usually oxygen evolution, takes place at a much higher potential as shown by the dotted line in Figure 13. However, in potentiostatic experiments on the same electrode, it is observed that beyond $E$ or $G$, the rate of the anodic reaction decreases as the potential becomes more positive. In Figure 13 the solid curve, obtained potentiostatically, shows that from $G$ to $I$ the current density decreases as the potential increases. From $I$ to $J$ the net anodic current is practically independent of potential and
Fig. 13. Ideal Galvanostatic and Potentiostatic Polarization Curves of Anodic Processes on a Metal Electrode.
at potentials more positive than J the current again increases in a logarithmic manner until oxygen evolution occurs. The decrease observed in the rate of dissolution is due to the formation of a protective surface film, probably an oxide. In the potential range from I to J the metal is passive and the dissolution rate, characteristic of the film, is from a thousand to a million times less than it is at E.

To study the passive behavior of an electrode, the potential rather than the current must be controlled. By convention, the potential is considered as the independent variable to be plotted on the abscissa and the current or current density is considered as the dependent variable to be plotted on the ordinate. In these experiments the current is related to the direction and magnitude of the reaction taking place at the surface of the electrode. An electrical device which controls the electrode potential is known as a potentiostat. All potentiostats operate on the same principle in that the potential difference between the working electrode and a suitable reference electrode is continually compared with the voltage derived from a potentiometer. The difference between the two, the error signal, is amplified and used to control the current passing through the electrolytic cell in such a way that the error signal is minimized. Potentiostats are characterized by the magnitude of the error signal, response time, power, and current
output and by its stability over a relatively long period of
time. The internal resistance of the instrument must be low
and its input impedance high to allow use of an external
reference electrode and a Luggin capillary which may have a
resistance of several thousand ohms. Leads to the electro-
chemical cell are shielded and kept as short as possible to
avoid stray potentials. Also, the working electrode is kept
at ground potential.

At present most potentiostats are electronic. How-
ever, it is possible to use an ordinary potential-divider
provided that the resistance of the bridge is sufficiently
low. A circuit, similar to that used by Greene (24) is
illustrated in Figure 14. When the resistance of the
circuit is low, reactions in the cell will not affect the
applied potential. A potentiometer, connected at E, is
employed to measure the potential drop at the surface of the
anode relative to a saturated calomel electrode.

In the absence of any applied current the local
anodic reaction

\[
\frac{nH_2O}{M} \xrightarrow{M^{+2}} nH_2O + 2e^- \quad (157)
\]

is balanced by the evolution of hydrogen on local cathodes

\[
2H^+ + 2e^- = H_2 \quad (158)
\]
Fig. 14. Potentiostatic Circuit for Determining Polarization Curves.
i.e., for a metal immersed in an acid solution. When both reactions occur at an equal rate there is no current flow because the partial currents are opposed and their sum is zero as illustrated by Schwarz (28) in Figure 15. At potentials more negative than A, hydrogen is evolved on the metal and at potentials more positive than B, anodic dissolution occurs. The value of potential A is determined by the overvoltage of hydrogen on a given material. Prazak (29) states that it becomes more positive with lower hydrogen overvoltages but, as a limit, can move only to the theoretical value of the hydrogen electrode potential at a given pH. Potential B, on the other hand, is more positive for metals which are electrochemically more noble. The overpotential and electrochemical response of the electrode is influenced by alloying elements and impurities present in the solution. A change in the physical composition of the system may have a favorable affect on the corrosion behavior of materials in the active state. For example, if potentials A and B are sufficiently far apart, the depolarization reaction of the corrosion process, i.e., the evolution of hydrogen, can only take place at potentials which are so negative that a very limited amount of anodic dissolution occurs. This behavior is exhibited by alloys rich in nickel. In addition, if potential B is equal to or more negative than potential A, as a result of hydrogen depolarization, then
Fig. 15. Partial Currents of Anodic and Cathodic Reactions Near Equilibrium Potential.
corrosion can take place at an apparently zero current. This is true for chromium and chromium-manganese alloys which exhibit poor corrosion resistance in the active state.

If the potential is moved in the positive direction, so as to make the electrode an anode, the dissolution reaction is stimulated while the cathodic reaction is diminished. When hydrogen evolution has ceased, the corrosion rate is proportional to the strength of the anodic current in agreement with Faraday's law. The current continues to increase with potential as shown by section ABCD of the curve in Figure 13. This region of the polarization curve is similar for all metals under suitable conditions and is indicative of logarithmic or Tafel behavior. At point C, inhibition of the anodic process takes place due to concentration polarization and the curve deviates from true Tafel behavior. From C to E, the concentration of metal ions on the surface of the electrode increases, until at F, conditions are conducive for the occurrence of a secondary reaction which leads to the formation of an interfacial compound. Because the new phase must be nucleated there is always a lag in the formation of crystallites, consequently the shape of this part of the curve depends on the rate at which the potential is increased. When the potential rise is very rapid the current density will increase to a maximum and then, due to supersaturation, will
fall to some low value, characteristic of the rate of increase in the potential. The current density will rise again to a steady value at which time the rates of formation and dissolution of the film are exactly balanced. The net current flow is nearly constant and independent of potential, thus the rate of dissolution of the film is diffusion controlled.

At point G there is a thermodynamic possibility for the formation of a protective film whether it is an oxide or merely an adsorbed layer of oxygen or hydroxyl ions. In all probability point G corresponds to the equilibrium potential or, as often referred to in the literature, to the Flade potential. By definition, the Flade potential is actually the equilibrium potential of the reverse process, i.e., the activation of the passivated metal. Nevertheless, the Flade potential, for the case of the forward course of the anodic polarization curve, should be identified with the equilibrium potential for the beginning of the formation of the protective film (30). If the overvoltage for the film-producing reaction is very small and the rate of chemical dissolution of the film insignificant, then the potential at point G will be very close to the observed Flade potential. For metals which do not exhibit a horizontal section in the active region, point G coincides with point E and a single maximum occurs in this section of the anodic polarization curve. Beyond point G the rate of anodic growth of the film
begins to exceed the rate of chemical dissolution, until at point H, the passivation potential, the electrode has a tendency to exhibit spontaneous passivation. As the areas of the passivated surface grow larger the anodic dissolution current decreases as shown by section HI. At point I the formation of the passive film is completed and the entire surface of the electrode is covered by a nonporous protective film. Over the potential range, I to J, the current flow is very low, only being sufficient to replenish the ions lost through the direct dissolution of the protective film by the electrolyte. The magnitude of the passive current density and the potential range over which passivity exists is indicative of the stability of the film. In some cases the rate of chemical dissolution of the passive layer is not entirely independent of potential. For example, as the potential and consequently the electric field increases, the passage of cations through the protective film in one direction and anions in the opposite direction increases, causing the thickness of the film to change accordingly.

At potentials more positive than J the current density rises as a logarithmic function of potential. This is the region of transpassivity which appears as a sloping line, JK, in which anodic dissolution takes place through the formation of soluble metal cations of higher valency. Prazak (29) observed that steel containing molybdenum and
chromium are most susceptible to dissolution in the trans-passive state. At more positive potentials a dip, KIM, in the anodic polarization curve appears. This region of secondary passivity is ascribed to the adsorption of oxygen at potentials just prior to the evolution of oxygen in the gaseous form. Metals which do not exhibit transpassive dissolution and secondary passivity usually serve as inert electrodes for the decomposition of water at potentials more positive than $J$.

The correlation between the shape of the potentiostatic polarization curve and the corrosion properties of an alloy can be successfully utilized if full cognizance is given to experimental limitations and to the theoretical principles governing irreversible electrode behavior. For example, it is known that the chemical effects of an environment can cause spontaneous passivation if its redox potential is more noble than the passivation potential of the metal. If the passivation potential of the metal is decreased by a judicious choice of alloying elements, then an environment with a relatively low redox potential will be sufficient to passivate the alloy, provided the redox reaction is capable of sustaining a flow of current greater than the maximum current density in the active range until the metal becomes passive. The possibility of this occurring
is improved by increasing the concentration of reducible components in the solution.

Another area of the polarization curve, characteristic of the corrosion resistance of a metal in a given environment, is the passive range. Beyond the passivation potential conditions are established which make possible the spontaneous formation of a stable protective film on the exposed surface of the specimen. The film continually undergoes dissolution and repair as indicated by the small but significant corrosion current in the passive range. The magnitude of the passive current density and the potential range over which passivity exists is indicative of the stability of the film. This is of utmost importance in systems employing anodic protection as a means of corrosion control.

At higher potentials the passive film breaks down and the measured current increases. It is thought that the presence of chromium and molybdenum facilitate film dissolution. Although few environments exist which are capable of producing such a high oxidation potential it is desirable that the transpassivation potential be as high as possible. But areas of transpassivity and secondary passivity are very sensitive to changes in composition of chromium-containing alloys. The shape of the anodic polarization curve at high
potentials is useful for alloy identification and for metallographic practice (31).

The region of secondary passivation is obtained only by supplying a high external current to the electrochemical system. This property is unimportant from a practical point of view since the state of passivity is relatively unstable and corrosion still takes place at a considerable rate.

According to Frazak (29), a potentiostatic polarization curve provides a graphic summary of the corrosion characteristics of a material in a given environment. Its plot and evaluation may be used as a very rapid and practically nondestructive corrosion test. It is particularly useful for the determination of fundamental corrosion properties. These results can be applied to a program concerned with the development of experimental alloys. Finally, it can be used to substantiate certain principles developed in the theory of electrode kinetics and as an aid in understanding the complex phenomena of metal passivity.
A. Specimen preparation

Specimen preparation is an integral and important part of any electrochemical experiment. A number of precautions are essential to ensure reproducible results. A brief description of the materials and methods used in melting and fabricating experimental alloys is presented.

The materials used in this study may be classified in two general groups—

1. Specially melted high purity alloys covering a wide range of iron, chromium and nickel compositions, which contain a selected number of fourth-component additions, and

2. Standard commercial alloys which have the same general compositional range as the specially melted alloys.

All materials are clearly marked in the iron-chromium-nickel ternary diagram reproduced in Figure 16. Binary and ternary alloys are designated with circles. Those alloys containing a fourth component are designated by diamonds. The fourth-component additions have been selected as those elements which commonly occur as impurities or are often added intentionally to iron-chromium-nickel base-alloys. The location of the coordinates for the fourth-component elements is based on the composition of widely used alloys.
LEGEND

- Two or Three Component Alloys from Pure Starting Stock
- Nitrogen Additions
- Commercial Alloy (Composition Noted for Reference)

Fig. 16. Isotherm of Iron-Chromium-Nickel Alloy System at 400°C Showing Alloys Selected for Experimental Studies.
Specifically, specimens of pure iron, pure chromium, pure nickel, and ten iron-rich iron-chromium-nickel alloys containing up to 20 per cent chromium and 20 per cent nickel are used in this investigation. Also included are ten fourth-component Fe-20Cr-15Ni base-alloys and a number of commercial grades of stainless steel. The latter group is employed to facilitate interpretation of experimental results and also because of their general industrial usefulness.

Fourth-component alloying additions were made at one location in the ternary diagram. To provide the most useful information on the effect of alloying only those elements which exhibit appreciable solid solubility in iron-chromium-nickel are used. Table 2 lists the alloying elements which were added and also their respective solid solubilities in \( \alpha \)-iron, \( \gamma \)-iron, pure nickel, and pure chromium. Each of the elements listed in Table 2 were added to Alloy 54 (refer to Figure 16) of base composition Fe-20Cr-15Ni at the 1.5 atomic per cent level. In addition carbon, oxygen, nitrogen, phosphorous, and sulfur were added to Alloy 54 at the 0.1 atomic per cent level.

The compositions of all experimental materials which include fourth-component alloys and commercial alloys are listed in Table 3.
<table>
<thead>
<tr>
<th>Element</th>
<th>Solubility (Atomic Percent) (^2)</th>
<th>Distance of Closest Approach (Å) (in temp. range of interest)</th>
<th>Crystal Structure</th>
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<td>Copper</td>
<td>(3) 7.5 100 0</td>
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<td>fcc</td>
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<td>Manganese</td>
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<td>cubic</td>
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<td>2.725</td>
<td>bcc</td>
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<td>Platinum</td>
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<td>fcc</td>
</tr>
<tr>
<td>Silicon</td>
<td>10 4 10 (5)</td>
<td>2.351</td>
<td>cubic</td>
</tr>
</tbody>
</table>


\(^2\) Numbers in parentheses are based on dotted lines or less certain data.

\(^3\) Taken at 400°C.

\(^4\) Taken at maximum.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Components, Weight Percent</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Other</th>
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</tr>
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<tr>
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<td>(20.80)</td>
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<td>--</td>
</tr>
<tr>
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</tr>
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<td>--</td>
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<tr>
<td>53</td>
<td>70.80</td>
<td>19.00</td>
<td>10.20</td>
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<tr>
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<td>54-Cu</td>
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<td>(1.71Cu)</td>
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<tr>
<td>54-Si</td>
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<tr>
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<td>Cr</td>
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<td>Bal.</td>
<td>22.38</td>
<td>13.54</td>
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</tr>
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</table>

1Numbers in parentheses refer to nominal alloy compositions.

2Iron by difference.

3Analysis by American Steel and Wire.

40.048N, 0.037C, 1.50 Mn, 0.019P, 0.016S, 0.45Si, 0.09Mo.

50.04N, 0.108C, 1.75Mn, 0.026P, 0.004S, 0.39Si, 0.21Mo.
The compositions of all experimental materials were homogenized, since impurities are known to influence electrochemical behavior. As an intermediate step, master alloys, which necessitated a second melting and consequently an additional purification step, were prepared from relatively pure stock material. As a result the impurity level in each of the final ingots is nearly identical.

Initial stock material used in the preparation of special binary master alloys include Ni-270 from International Nickel, ELECHROME from Union Carbide, and 104 Iron from the Glidden Company. The compositions of these materials are given in Table 4. They were selected as a compromise between cost and quality. It was concluded that there was little incentive to purchase material of higher purity since the impurities listed in Table 4 were substantially reduced during vacuum melting. The iron and chromium were shipped in the form of irregular electrolytic platelets and the nicel as 0.3125 inch rod.

Five binary master alloys were prepared by the Battelle Memorial Institute in 20 pound ingots by vacuum induction melting. This procedure was followed to reduce the level of volatile impurities such as nitrogen, oxygen, and carbon (as CO) to less than 100 ppm and to homogenize nonvolatile impurities. Results of chemical analyses are listed in Table 5. Comparing the information in Tables 4
<table>
<thead>
<tr>
<th>Impurity</th>
<th>Glidden 104 Iron</th>
<th>270 Nickel</th>
<th>Elchrome Chromium</th>
</tr>
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<tr>
<td>Carbon</td>
<td>50</td>
<td>200</td>
<td>80</td>
</tr>
<tr>
<td>Oxygen</td>
<td>500</td>
<td>22</td>
<td>130</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>40</td>
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</tr>
<tr>
<td>Nitrogen</td>
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<td>12</td>
<td>100</td>
</tr>
<tr>
<td>Sulphur</td>
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<td>30</td>
<td>60</td>
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<td>Phosphorous</td>
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<tr>
<td>Cobalt</td>
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<td>30</td>
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<tr>
<td>Chromium</td>
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<td>Copper</td>
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<td>Iron</td>
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<td>Silicon</td>
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<tr>
<td>Titanium</td>
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</table>

\(^1\)Impurity content given in ppm.

\(^2\)Vacuum fusion analysis by Battelle Memorial Institute. All others were furnished by Vendor.
### TABLE 5
COMPOSITION OF MASTER ALLOYS

<table>
<thead>
<tr>
<th>Alloy Melt Number</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>O</th>
<th>H</th>
<th>N</th>
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<td>1</td>
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<tr>
<td>2</td>
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<td>.0110</td>
<td>.0028</td>
<td>.00004</td>
<td>.0020</td>
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<tr>
<td>3</td>
<td>71.25</td>
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<td>.0050</td>
<td>.0100</td>
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<tr>
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<td>4.88</td>
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<td>.0027</td>
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<tr>
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<td>15.13</td>
<td>.0060</td>
<td>.0035</td>
<td>.00004</td>
<td>.0020</td>
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</tbody>
</table>

1Analyses by The Duriron Company, Dayton, Ohio for Iron, Chromium, Nickel using X-ray quantometer and wet chemical. Interstitial analyses by Battelle Memorial Institute: Oxygen and hydrogen by vacuum fusion. Nitrogen by Kjeldahl technique.

and 5, it is apparent that considerable reductions have been made in carbon, oxygen, and nitrogen levels. This has been achieved by vacuum induction melting and by making appropriate additions of carbon (as iron carbide) or additions of oxygen (as iron oxide). It should be noted that in several cases the oxygen or carbon is relatively higher than average, however these were reduced when ingots of specific composition were prepared from the master alloys.

After melting, the master alloys were forged, hot rolled to plate, and sheared into small pieces suitable for remelts.
With the exception of alloys containing both high chromium and high nickel, a forging temperature of 2000°F was satisfactory.

Selected alloys to be studied were vacuum induction melted in high purity magnesia crucibles with excess additions of carbon. These crucibles were chosen because magnesium, which is produced by the reduction of magnesia by carbon, is volatile and would not be expected to remain in the melt. Furthermore, excess carbon, by combining with oxygen in the melt, volatilizes as carbon monoxide. In order to obtain the maximum possible deoxidation or carburization of the melt, additions of oxygen as Fe$_2$O$_3$ and carbon as Fe$_3$C were made when necessary. Charge compositions are given in Table 6.

Following melting, the heats were vacuum cast into copper molds. An ingot of 85 per cent nickel and 15 per cent chromium was examined in cross-section to study freezing patterns. In general the grains grew straight to the axial centerline of the ingot indicating no vertical segregation. Ingots which were radiographed in the Department of Welding Engineering at The Ohio State University indicated some centerline shrinkage cavities. Examination of the ingots, however, revealed no contamination on the internal surface of the defect and it was assumed that these cavities would close during fabrication and become metallurgically bonded.
### TABLE 6

**CHARGE COMPOSITIONS**  
*(Weight in grams)*

<table>
<thead>
<tr>
<th>Alloy Number</th>
<th>Fe</th>
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<th>Cr</th>
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<th>4</th>
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<td>608 11.3Cu</td>
</tr>
<tr>
<td>54-Mn</td>
<td>--</td>
<td>--</td>
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<td>--</td>
<td>--</td>
<td>--</td>
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<td>--</td>
<td>--</td>
<td>608 9.0Mn</td>
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<tr>
<td>54-Mo</td>
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<td>--</td>
<td>--</td>
<td>603 16.4Mo¹</td>
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<tr>
<td>54-N</td>
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<td>--</td>
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<tr>
<td>54-O</td>
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<td>--</td>
<td>--</td>
<td>618 .65Fe₂O₃</td>
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<tr>
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<td>--</td>
<td>618 2.0Fe₃P</td>
</tr>
<tr>
<td>54-Pt</td>
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<td>--</td>
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<td>--</td>
<td>--</td>
<td>586 33.5Pt³</td>
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<tr>
<td>54-S</td>
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<td>--</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>618 1.18FeS</td>
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<td>54-Si</td>
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<td>--</td>
<td>614 5.0Si</td>
</tr>
<tr>
<td>55</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>308</td>
<td>154</td>
<td>--</td>
<td>162</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

¹Charged as arc-melted alloy button.
²Chromium--1.63 w/o nitrogen alloy.
The one pound ingots had a usable section of 5.5 inches in length and 0.7 inch in diameter. The actual weight of material available in each ingot for fabrication was 0.8 to 0.9 pounds. All alloys were processed in an identical manner to reduce uncertainties due to prior history. Based on results from a preliminary fabrication study, the ingots, except for pure chromium, were reduced by hot rolling in eight steps down to 0.260 inches in diameter at a temperature of 2200°F. Intermediate fabrication was performed at Battelle Memorial Institute. In general, the alloys were reheated every two passes which constituted one reduction in size. In the second pass through each size the rod was rotated 90 degrees from the first. At the 0.625 inch, 0.438 inch, and 0.250 inch sizes the alloys were grit blasted and all defects removed by grinding. Since it was neither practical nor economical to use an inert gas all heating for hot rod rolling was done in air. After pickling to remove the scale, the material was given a final anneal at 2000°F for 15 minutes. No difficulty was experienced in fabricating any of the alloys tested.

As a final preparation, cylindrical samples of the annealed high purity iron-chromium-nickel alloys were carefully machined into 0.25 inch diameter rods. A 1 inch section of each rod was set into a specially prepared Teflon mount which held the sample tightly. Electrical contact was
achieved through an opening in the top of the mount into which one end of a stainless steel rod was inserted and fastened to the specimen. A thin Teflon jacket was slipped over the electrical lead and screwed into the Teflon housing, thereby providing a leak-proof seal. The entire electrode assembly is shown in Figure 17. This design meets all the requirements deemed essential in electrochemical studies, i.e., it provides air and liquid tight seals, it is non-contaminating, it is adaptable to varying environments and temperatures, and it is simple to clean and to assemble.

The mounted specimen was then ground to a 600-grit finish through a series of metallographic papers and dipped into Cleaning Solution prior to the beginning of the experiment. Both cathodic and chemical activation treatments were tried. The latter proved more successful in rendering the surface of all materials active. The treatment consisted of a 5 minute immersion in boiling In H2SO4 after which the electrode was assembled, flushed with conductivity water, and immediately transferred to the cell.

B. Electrolyte

Sulfuric acid was chosen because it is the simplest electrolytic solution which demonstrates the phenomenon to be studied, i.e., the active-to-passive transition characteristic of iron-chromium-nickel alloys. Thus, measurements
Fig. 17. Electrode Assembly.
can be made which are indicative of the stability of passive films. Sulfuric acid solutions are also relatively free of complex ions and are only slightly oxidizing in nature (32). In addition, this choice greatly simplified interpretation of experimental measurements because of the large amount of information already available on the behavior of this alloy system.

In any electrochemical experiment certain rules of cleanliness must be observed. The degree of purity required in each particular case is dependent upon the characteristics of the system, the use to which the results will be applied, and the required accuracy of the measurements. As pointed out by Greene (24), the purification technique should be maintained as simple as possible and should be consistent with accurate interpretation and experimental reproducibility. In accordance with these suggestions the following techniques were employed in the preparation of electrolytic solutions.

With the exception of a few specific tests, the majority of the experimental work was carried out in 1N H₂SO₄. This solution possesses adequate conductivity without the addition of a supporting electrolyte. The specific conductance of 1N H₂SO₄ at 20°C is reported equal to 0.21 Mhos by the Engineering Department of Industrial Instruments Incorporated (33).
The determination of Flade relations for specially prepared pure iron, chromium, and nickel electrodes required a variation in solution pH. Consequently, it was necessary to change the composition of the environment. To accomplish this change with a minimum of diversity in experimental conditions the strength of the electrolytic double layer and the activity coefficient of the electrolyte was held constant (9). In dilute solutions the activity coefficient is determined by the ionic strength of the

\[
I = \frac{1}{2} \sum m_{i}n_{i}^2
\]

(159)

where \(m_{i}\) is the molality and \(n\) is the electrical charge of the ions. The summation is taken over all the different ions in solution. According to equation (159) the total concentration of ions of equal charge must be held constant.

Since the hydrogen ion concentration in a 1N \(H_2SO_4\) solution is equal to unity, an addition of potassium sulfate must be added to more dilute solutions in order for the total concentration of monovalent cations to equal unity. The lower the hydrogen ion concentration the higher the potassium ion concentration. Consequently, the concentration of bivalent sulfate ions must also be constant. Ionic concentration and pH values for the various solutions employed in this experiment are listed in Table 7.
TABLE 7

COMPOSITION AND pH OF ELECTROLYTIC SOLUTIONS

<table>
<thead>
<tr>
<th>Normality</th>
<th>pH(^a)</th>
<th>Grams</th>
<th>[H(_2)SO(_4)]</th>
<th>[H(^+)]</th>
<th>[SO(_4^{2-})]</th>
<th>Grams</th>
<th>[K(_2)SO(_4)]</th>
<th>[K(^+)]</th>
<th>[SO(_4^{2-})]</th>
<th>Grams</th>
<th>H(_2)O</th>
<th>H(_2)SO(_4)-96.3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.90</td>
<td>49.041</td>
<td>0.513</td>
<td>1.026</td>
<td>0.513</td>
<td></td>
<td></td>
<td></td>
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<td>1000</td>
<td>27.68</td>
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<td>0.1</td>
<td>1.86</td>
<td>4.904</td>
<td>0.050</td>
<td>0.100</td>
<td>0.050</td>
<td>80.686</td>
<td>0.463</td>
<td>0.926</td>
<td>0.463</td>
<td>1000</td>
<td>2.77</td>
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</tr>
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<td>0.01</td>
<td>2.52</td>
<td>0.490</td>
<td>0.005</td>
<td>0.010</td>
<td>0.005</td>
<td>88.528</td>
<td>0.508</td>
<td>1.016</td>
<td>0.508</td>
<td>1000</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>2.65</td>
<td>0.049</td>
<td>0.0005</td>
<td>0.001</td>
<td>0.0005</td>
<td>89.312</td>
<td>0.513</td>
<td>1.025</td>
<td>0.513</td>
<td>1000</td>
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<td>89.399</td>
<td>0.513</td>
<td>1.026</td>
<td>0.513</td>
<td>1000</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Experimental determination.
All solutions were prepared with triple-distilled water and reagent grade sulfuric acid. Since trace amounts of organic impurities are detrimental to potential measurements the last distillation treatment was performed over alkaline permanganate. The distilled water and experimental solutions were stored in pyrex glass vessels to avoid contamination. The specific conductance of the water was 0.99 micro-mhos at 18°C.

Oxygen was eliminated from the electrolyte since it contributes one more redox system to be considered. This was accomplished by purging the solution in the cell with hydrogen gas containing less than 0.5 ppm oxygen and a total hydrocarbon content of 0.2 ppm for a 12 hour period. Hydrogen was used in preference to nitrogen or to one of the rare gases since it tends to establish a steady-state hydrogen redox potential.

In addition to removing oxygen from the cell the solution was pre-electrolyzed for 12 hours by applying a potential of 2 volts across two cylindrical platinized platinum electrodes. If time is not essential it is preferable to pre-electrolyze in the test cell because impurities entrapped in the walls of the vessel may contaminate the solution if they are not removed in the purification treatment.
C. Polarization test cell

All electrochemical measurements were obtained by using the two compartment pyrex glass cell shown in Figure 18. The 500 and 150 milliliter capacity compartments, containing the anode and cathode, respectively, were separated by a fine porosity, fritted glass disk. This gave a good separation of anode and cathode reaction products and allowed control of the gaseous environment in each compartment. Accommodations for an auxiliary electrode, a hydrogen electrode, and a thermometer were provided in the anode compartment. Deaeration was accomplished by passing high-purity hydrogen into each compartment of the cell through coarse fritted glass dispersion tubes. The hydrogen was passed through the solution or by-passed over the top by turning appropriate stopcocks. A slight positive pressure was maintained in the vessel by emitting the gas through water traps which were an integral part of the electrode assemblies. All fittings were constructed of Teflon or pyrex glass and no lubricant was employed.

Since all tests were conducted in unstirred solutions the anode was mounted horizontally so that the products of electrochemical reactions could be removed more effectively by natural convection forces. In this position, the face of the anode could be placed immediately in front of the Haber-Iuggin probe which entered the cell at a 45 degree
Fig. 18. Pyrex Glass Cell Used in Electrochemical Measurements.
angle. The probe was constructed from a short length of pyrex glass tubing, drawn at one end to a fine capillary tip less than 1 millimeter in diameter and fitted at the other end with a small spherical glass joint. An inverted L-shaped piece of glass tubing containing a stopcock at one end was coupled to the probe to complete the solution bridge. The probe, as well as the anode assembly, could be raised or lowered at will through Teflon seals so that the capillary tip could always be brought up to the surface of the corroding specimen. In addition, the mounting technique permitted numerous tests to be run on one sample. By simply removing the affected surface area of the sample following each experiment, the electrode and probe could be lowered further into the cell and placed in the most desirable position.

Upon completion of the purification treatment the probe was filled with solution syphoned from the anode compartment of the cell. The other end of the solution bridge was securely fastened to a bottle containing a saturated solution of potassium sulfate which was interconnected by an agar bridge to a second bottle containing a saturated solution of potassium chloride. A fine fritted glass disk was used at the end of the solution bridge to prevent excessive flow of the saturated potassium chloride solution into the cell. A saturated calomel electrode was placed in the
second bottle. These precautions were taken to minimize the adverse effects of an unknown liquid junction potential. The agar gel was made by dissolving 2 grams of agar into a 100 milliliter solution of boiling saturated potassium chloride. It was immediately transferred to the bridge and quickly cooled in running water. The gel cleared upon solidification and showed visible crystals of potassium chloride in suspension.

The metallic base for the hydrogen electrode, cathode, and auxiliary electrode was platinized platinum. The spiral-shaped hydrogen electrode, constructed of 20 gage platinum wire, had an area of 7.1 square centimeters. Both the cathode and auxiliary electrode were made of 0.005 inch platinum foil. They were cylindrical in shape and had a total surface area of 25.30 square centimeters. Prior to platinization the electrodes were cleaned by brief immersion in warm aqua regia. This solution was also employed for stripping the platinum black from used electrodes. The platinum black was deposited from a per cent solution of chloroplatinic acid containing a 0.2 per cent lead acetate. A current density of 50 milliamperes per square centimeters was passed between two electrodes in the platinizing cell for five 1 minute periods, being reversed after each period, until the platinized surface attained a black velvety appearance. Reversing the direction of current flow
minimized the amount of occluded gas in the deposited platinum.

After the above treatment the electrodes were cleaned by electrolyzing at a current density of 50 milliamperes per square centimeters solution of 10 per cent H₂SO₄. This was accomplished by electrolyzing for five 1 minute periods and reversing the current flow at the end of each period.

In the final step, the platinized electrodes were copiously rinsed with tripled-distilled water and stored in specially prepared flasks to prevent contamination from atmospheric dust and unnecessary handling.

D. Constant potential apparatus

All electrochemical measurements were carried out under constant potential conditions because of the thermodynamic background of the phenomena to be studied. The potential was considered primarily as the independent variable, and the current or current density, which is directly related to the direction and extent of the reactions taking place, as the dependent variable. A working electrode, a reference electrode, and an inert auxiliary electrode were required to operate the cell under potentiostatic conditions. All tests were conducted with the Model 4100 Research Potential Controller (34).

Briefly, the potential controller or potentiostat is an electronic device which is capable of detecting and
correcting a change in the potential difference between the working electrode and the reference electrode by continually comparing the difference with the voltage derived from a potentiometer. Such changes occur as a result of reactions taking place in the polarization cell.

An outline of the system used in the experimental program to study the relationship between electrode potential and corrosion rate is presented in Figure 19. The working electrode is polarized to the desired potential by passing a current between it and the auxiliary electrode. At the same time, the potential of the working or test electrode is measured with respect to the potential of the reference electrode which is assumed constant under given experimental conditions. The large block in the diagram represents the electronic potential controller. It must have a low internal resistance and a high input impedance to allow use of a high-resistance reference electrode and a Luggin capillary which may have a resistance of several thousand ohms.

An enlarged block diagram of the Model 4100 Research Potential Controller is given in Figure 20. The incoming reference electrode voltage is applied to the center point of a bank of mercury cell batteries. An opposing voltage is developed between this center point and the center arm of the potential control potentiometer. In operation, the
Fig. 19. Outline of System for Studying the Relationship between Electrode Potential and Corrosion Rate.
Fig. 20. Block Diagram of Model 4100 Potential Controller.
desired potential, derived from the potentiometer, is preset into the potential control circuit in electrical opposition to the potential difference, \( E \), between the reference auxiliary electrodes. The sum of their values is a subtraction process and the difference is termed the error signal. The control amplifier expands the error signal and converts it to a control signal which is used to regulate the current passing through the electrolytic cell in such a way that the error signal is minimized. The sole purpose of the electronics is to make the error signal zero. When this occurs the potential developed between the reference electrode and the working electrode is exactly equal to the voltage preset into the potential control circuit. Because of the extremely high input impedance essentially no current is drawn through the reference electrode and its potential remains stable. The necessity of maintaining short lead lengths has been eliminated by the development of a unique grounding system in this circuit.

The Model 4100 Research Potential Controller is designed to maintain a constant potential with \( \pm 1 \) millivolt over the range 0 to \( \pm 5.0 \) volts. The meter provided for reading this control potential has two scales: 0 to \( \pm 1 \) in 40 millivolt steps and 0 to \( \pm 5 \) volts in 200 millivolt steps. Since the resolution of the meter was less than that desired an external digital voltmeter, Hewlett-Packard Model 3400A
was utilized. The voltmeter has a dc accuracy of better than $\pm 0.05$ per cent of reading $\pm 1$ digit over the ambient temperature range of $+15^\circ C$ to $+40^\circ C$ with a line voltage variation of $\pm 10$ per cent. An additional feature which results in high accuracy is the constant 10.2 megohm impedance. This impedance presents a constant load on all voltage ranges. Use of the Hewlett-Packard Model 3441A Range Selector in conjunction with the digital voltmeter permitted a selection of three voltage ranges, 9.999, 99.99, or 999.9 volts, to be made with a resolution of 1 millivolt on the 10 volt dc range.

Other features of the electronic potentiostat are--

1. A sensitivity of $\pm 0.5$ millivolts,

2. A stability of less than $\pm 1$ millivolt after a 30 minute warm-up period,

3. A rated current capacity of 15 amperes anodic or 2.5 amperes cathodic, and


The ammeter built into the controller has the following scales--

1. 0 to 100 microamperes,
2. 0 to 1 milliampere,
3. 0 to 10 milliamperes,
4. 0 to 100 milliamperes,
5. 0 to 1 ampere, and
6. 0 to 10 amperes.

A shunt position is also incorporated into the control switch by which the panel current meter can be by-passed and
the full current output registered on a 0-100 millivolt recorder. Jacks are provided in the rear of the instrument for recording each full-scale current and potential range.

It is possible to set this controller to scan from a preset potential "A" to a preset potential "B" over varied periods of time. A motor drive can be easily incorporated to provide a long scan time of extreme linearity.

Current and potential measurements were plotted automatically with a Bristol Model 560 High-Speed (0.4 seconds) Dynamaster potentiometric recorder. A unique arrangement of electrical relays coupled to the potential controller provided a wide choice of potentiodynamic measurements. The significant characteristics of the experimental apparatus was its ability to record current over six orders of magnitude. Current resolution was 0.1 microampere and if necessary potentials could be read to within 1 millivolt.

E. Determination of a polarization diagram

At the beginning of each experiment the cell and all auxiliary components were cleaned with a chromic-sulfuric acid solution and copiously rinsed with triple-distilled water. The equipment was then immersed into an electrically grounded constant temperature bath. To maintain uniformity of results the temperature was automatically controlled to
within ±1°C. Initially, tests were conducted at 25°C, 50°C, and 75°C in an effort to determine the effect of temperature on the position and shape of the anodic polarization curve. The temperature, however, for the remainder of the experimental program was maintained at 25°C ±1°C.

Immediately after the cell was in position it was filled with approximately 650 milliliters of electrolyte and fitted with the thermometer, Luggin probe, and auxiliary electrodes. The large central joint for introducing the sample was closed at this time. Next, Tygon tubing was attached to the bottom and top of the cell for the entrance and exhaust of the gas. Following this, the hydrogen was bubbled vigorously through the electrolyte for approximately 12 hours to deaerate and to saturate the environment. In addition, the solution was pre-electrolyzed by applying a potential of 2 volts across the cylindrical platinized platinum electrodes for the same length of time.

Upon completion of the purification treatment the specimen was chemically activated and immediately lowered into the electrolyte with its surface positioned adjacent to the tip of the Luggin probe. The conductivity bridge was filled with solution syphoned from the anode compartment of the cell. The agar bridge and calomel electrode were then set into position.
The reversible hydrogen potential of the acid solution was measured with respect to the saturated calomel electrode using a Rubicon Potentiometer. For pH measurements a stream of oxygen-free hydrogen gas was allowed to bubble through the solution in the vicinity of the spiral-shaped platinized platinum electrode. The position of the electrode in the solution was arranged so that it was partly in the solution and partly in the atmosphere of hydrogen gas. This arrangement permitted the rapid attainment of equilibrium between the electrode material, the hydrogen gas, and the electrolyte. A steady potential was obtained within 1 to 5 minutes when the electrode was fresh. When a longer time was required the hydrogen and auxiliary electrodes were cleaned in aqua regia and replatinized. Following the establishment of steady-state the potential was recorded and the hydrogen gas by-passed over the top of the solution by turning the appropriate stopcocks.

Corrosion potentials were measured using a saturated calomel electrode maintained at the same temperature as the specimen. The open-circuit corrosion potential of the anode was monitored with a potentiometer until a steady-state value was obtained, usually this required 30 to 60 minutes. When the equilibrium conditions were established the potentiometer was disconnected and the leads from the potentiostat were affixed to the anode, cathode, and reference electrodes.
The following procedure was used to determine the polarization behavior of the specimen when the control potential was automatically shifted from a preset potential value "A" to a preset potential value "B." The open-circuit corrosion potential was preset into the potentiostat as control potential "A" using the external vacuum tube voltmeter. Similarly, the desired final control potential was preset into the potentiostat as control potential "B." The time for the potentiostat to shift from control potential "A" to control potential "B" was governed by a motor drive incorporated into the instrument. An appropriate selection of the scanning rate was resolved from the nature of the experimental program and the characteristics of the system being studied. For example, anodic polarization curves were determined on one alloy using scan speeds of approximately 50, 100, and 250 millivolts per minute. Current response was shown to vary over an order of magnitude depending on the rate of increase in applied potential. As a result of these findings a scan speed of about 100 millivolts per minute was utilized in the remainder of the investigation. By means of a high-speed potentiometric recorder and a unique arrangement of electrical relays the current and control potential were recorded automatically. The entire experimental apparatus is shown in Figure 21.
Fig. 21. Measuring and Control Equipment for Polarization Studies.
In some cases both anodic and cathodic polarization measurements were obtained on one sample. It was found that cathodic polarization did not appreciably affect the corrosion potential of an electrode after the applied current was stopped. Whereas, after prolonged anodic polarization the electrode would not return to its original steady-state. Cathodic polarization tests were therefore run prior to anodic polarization tests. The same scan rate was used in both cases.
V RESULTS AND DISCUSSION

A. Metallurgical structure

A metallographic study was conducted to determine the effects of heat treatment and composition on the microstructures of experimental materials. Since all the samples employed in this investigation were reheated after fabrication for 5 minutes at 2200°F to reduce uncertainties due to prior history, they were in the fully annealed condition. Metallographic examination revealed that the structures of the alloys were as follows:

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 27, 51, Cr</td>
<td>( \alpha ) (Ferritic)</td>
</tr>
<tr>
<td>3, 4, 29</td>
<td>( \alpha + \gamma )</td>
</tr>
<tr>
<td>12, 31, 53, 54, 55, 309</td>
<td>( \gamma ) (Austenitic)</td>
</tr>
</tbody>
</table>

The specimens were examined again after electrolysis, however no significant information was obtained. Grain boundary attack was evident on all alloys, and in some cases selective dissolution of the grains occurred on some of the samples due to orientation differences. As might be expected, pitting attack was evident on the exposed surface of the specimens. The pits were distributed uniformly throughout the grains and no correlation with structure was discerned.
B. Anodic polarization diagrams

The thermodynamic background to all corrosion problems makes it a logical choice to carry out any investigational work under constant potential conditions (21). Potentiostatic experiments are a completely satisfactory method of corrosion research provided the results they give are selective, reproducible, and capable of interpretation. These conditions are often difficult to obtain simultaneously, mainly because the variables which can affect the shape of a polarization curve obtained in a potentiostatic experiment depend upon the nature of the metal or alloy, on the characteristics of the solution, and on the method of investigation (35). Two techniques which are adaptable to polarization studies include potentiodynamic and potential-step measurements. The first method is accomplished by continuously changing the electrode potential at a constant rate while simultaneously recording current flow. In the latter method, the electrode potential is changed discontinuously in finite increments and the current is recorded after a predetermined time interval. In each case, the measured current is related to the direction and extent of the reactions taking place.

A detailed study of the experimental program resulted in the development of a potentiodynamic method which led to entirely satisfactory solutions of the problems considered.
Since this study is concerned primarily with the influence of alloying elements on the corrosion behavior of metals, the greatest importance of the technique does not lie in the final determination of the rates of corrosion, but rather in the rapid comparison of fundamental corrosion properties (29). This is particularly important in the evaluation of a series of experimental alloys.

1. Experimental variables

The shape of the polarization curve depends to some extent on the rate of change of the electrode potential because electrode reactions take a finite time to establish steady-state conditions. For example, it requires one week or more to reach steady-state passive currents on austenitic stainless steels (36). The measurement of steady-state polarization data, therefore, is not only tedious but may be undesirable. It was pointed out by Littlewood (37) that the polarization curve of an alloy obtained in a dynamic experiment might be influenced by at least three effects occurring during the course of the determination--

1. Changes of surface composition of the specimen due to preferential dissolution of one constituent,

2. Changes of composition in the solution due to the build-up of corrosion products, and

3. The supply of current required to thicken or to thin the oxide as the potential of the specimen was altered.
The first two effects are revealed either when polarization curves are obtained in experiments of long duration or when repeated determinations are carried out on the same specimen or in the same solution. On the other hand, the effects of film thickening can be expected to be most important when potential scanning is carried out rapidly and less important in experiments carried out at slow scan rates.

The diagram reproduced in Figure 22 illustrates the effect of scanning rate on the position and shape of the anodic polarization curve of an Fe-20Cr-15Ni alloy (Alloy 54) in 1N H₂SO₄ at 25°C. Traverse rates of 28.10, 84.40 and 251.64 millivolts per minute were used in the potentiodynamic measurements. All potential measurements were reported with respect to the saturated calomel reference electrode. Current response was shown to vary over an order of magnitude depending on the rate of change in applied potential.

In alloy development a technique of increasing the potential at a constant rate may be perfectly sound and comparison of the shapes of such curves may give all the information required. Nevertheless, a potential-step technique, properly applied, might be more easily correlated with the behavior of an alloy on its initial immersion in a solution. Littlewood (37) suggested that a new specimen and a fresh solution be used to obtain each point on the
Fig. 22. Effect of Scanning Rate on the Anodic Polarization Response of an Fe-20Cr-15Ni Alloy in 1N H$_2$SO$_4$ at 25°C.
polarization curve and to study carefully the current-decay characteristics at every potential.

In a similar investigation by Greene and Leonard (36) on the effect of experimental variables on potentiostatic anodic polarization measurements, it was concluded that automatic potentiodynamic techniques yielded the most reproducible results. Potential-step methods, on the other hand, were less consistent due to timing errors. Generally, it was observed that potentiostatic polarization characteristics were essentially controlled by the potential traverse rates and were found to be independent of the manner in which the electrode potential was varied. The appropriate selection of the scanning rate must therefore be determined by the nature of the experimental program and the characteristics of the system studied. However once a choice was made, it would be best to use it for the remainder of the investigation.

Equally important is the temperature at which the experiment is conducted as shown in Figure 23. The general shape of the curve remains constant, however, the rate of dissolution increases significantly with temperature. In Table 8 are given several of the values which are characteristic of the anodic response of Alloy 54 in 1N H₂SO₄ as a function of scanning rate and temperature.
Fig. 23. Effect of Temperature on the Anodic Polarization Response of an Fe-20Cr-15Ni Alloy in 1N H$_2$SO$_4$ at a Scanning Rate of 28.10 mv/min.
<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>pH</th>
<th>Scanning Rate, mv/min</th>
<th>Potential, mv (SCE)</th>
<th>Current Density, ma/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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**TABLE 8**

CORROSION OF Fe-20 Cr-15 Ni ALLOY IN 1N H₂SO₄
Since overvoltage is due to a slow stage in the dissolution process, it is evident that an increase in temperature will decrease overvoltage and stimulate the anodic reaction. As the temperature is raised, the diffusion coefficient increases and at the same time the thickness of the diffusion layer decreases. According to Glasstone (3), the influence of temperature on the thickness of the diffusion layer is somewhat uncertain, but experience suggests that the value at 75°C is about one-third of that at 25°C, in a stationary solution. In addition, the diffusion coefficient of most substances in aqueous solution increases by about 2.5 per cent per degree, this being the coefficient of decrease viscosity. It follows, therefore, that the limiting current is slightly over four times as great at 75°C as at 25°C. This increase is small compared with that which results from agitation of the solution. Agar and Bowden (18) observed that when the numerical value of the limiting current is increased, either by stirring or by increasing the temperature, concentration overpotential will fall. The ohmic potential drop in the diffusion layer is of the same order of magnitude and varies with the limiting current in the same manner. This unusual result is a consequence of the relation between the diffusion coefficient of an ion and its mobility. The limiting current density, on the other hand, has little or no affect on
activation overpotential. Despite this fact, the temperature coefficient of the latter process (2.5 millivolts per degree), under similar conditions is found to be considerably higher than the value for concentration overvoltage (0.5 millivolt per degree). The influence of temperature must therefore be inherent in terms of the energy of activation of the slow process responsible for activation polarization. Since the three main causes of irreversibility in electrode reactions are indirectly related to temperature, it is difficult to speculate on which particular process is rate controlling at elevated temperatures.

Variations in methods of specimen preparation are known to produce pronounced differences in the shape of polarization curves of alloys undergoing active-to-passive transitions. Experimentally, electrodes are prepared by an arbitrary technique and usually each worker adheres to one particular method. Resultant measurements are not universally applicable but are specific to the particular sample studied. Wide differences are often observed between samples of a given metal or alloy (37). Littlewood (37) attributed this to the previous history of the specimen and to the manner in which it affects the polarization curve by changing the cathodic characteristics of the electrode. Equally important is the surface pre-treatment. For example, in preliminary experiments an electropolished specimen was
found to give different results than a descaled specimen (37). In addition, cathodic pre-treatments have a marked effect on polarization-curve characteristics which become more pronounced with longer pre-treatment times and with more active pre-treatment potentials (36).

Specimens which are self-activated by the electrolytic solution would appear to yield the most reproducible results, provided prior metallurgical history may be neglected as a variable. Iron in dilute solutions of sulfuric acid satisfies the above requirement. Most grades of stainless steel, however, must be activated by other means, either chemically or cathodically. Organic solvents and most prepared chemical mixtures should be avoided since impurities foreign to the electrolyte may be adsorbed onto active sites on the surface of the specimen. Solutions differing in activity and composition from the chosen electrolyte should also be avoided since equilibrium conditions may be disturbed. The extent of deviation from reversibility depends upon the ratio of surface anode to cathode areas as the electrode is polarized. It is apparent in some cases that the total anodic area at any moment is probably much less than the cathodic area, even though anodes and cathodes may interchange relative positions as the reaction proceeds (38). An increase in the anodic area by chemical activation or by external anodic polarization produces a large percentage
increase of available anodic surface, but the change is sluggish, accounting in part for the marked hysteresis of anodic polarization data. The fact that hysteresis is less or is absent for corresponding cathodic polarization measurements, suggests that in at least some aqueous media, cathodic activation treatments are satisfactory.

Mounted specimens employed in this investigation were ground to a 600-grit finish through a series of metallographic papers prior to the beginning of the experiment. In lieu of the above, both cathodic and chemical activation treatments were tried, however the latter proved more successful in rendering the surface of all experimental materials active. Prolonged cathodic pre-treatments passivated the iron-chromium-nickel alloys as illustrated in Figure 24. The chemical activation treatment consisted of 5 minute immersion in boiling 1N H₂SO₄ after which the electrode was assembled and immediately transferred to the cell. Corrosion potentials were generally reproducible to within ±5 millivolts.

Finally the metallurgical condition of the specimen must be considered. This fact has already been adequately demonstrated (31). Aside from the effect on the over-all shape of the polarization curve due to the presence of phases of different composition in the alloy, the etching effect in particular might be expected to have considerable influence
Fig. 24. Effect of Activation Pre-treatment on the Anodic Polarization Response of an Fe-20Cr-15Ni Alloy in 1N H₂SO₄ at 25°C. (100 mv/min) (1) Chemically Activated (2) Electrolytically Activated.
in heterogeneous specimens. Corrosion and etching properties are closely related since the processes occurring in metallographic etching are actually corrosion processes. Both are dependent upon the solution composition and temperature, as well as on the chemical composition of the alloy and the type and number of different phases present. According to Prazak (26), it is possible to predict the approximate shape of the curve from the composition of the alloy and the solution in which it is immersed, and conversely the characteristics and composition of the alloy can be judged from a knowledge of its polarization curve.

The structure of stainless steel depends not only on the balance of the chromium and nickel contents but also on the proportion of additional elements. For example, it is known that nitrogen, carbon and manganese favor the formation of austenite, whereas molybdenum and silicon aid in the formation of delta ferrite. It has been reported, however, that the differentiation of phases in most iron-chromium-nickel alloys is based primarily on their differing chromium contents (31). Nickel, in amounts as high as 7 percent has no pronounced effect on the position of the characteristic regions of the curve on the potential axis and only gives a slight decrease in the rate of anodic dissolution in the active region.
In an attempt to define the polarization characteristics of ferrite and austenite in stainless steel, two special alloys, similar in composition, were prepared. Alloy 53, 19.00 Cr-10.20 Ni-0.007C, is austenitic, whereas Alloy NV-1, 16.89 Cr-9.09Ni-0.006C, is ferritic. The curves in Figure 25 illustrate the similarities in anodic behavior of the two samples. It is apparent that composition, rather than structure, is the predominate factor controlling the dissolution characteristics of iron-chromium-nickel alloys in dilute solutions of sulfuric acid.

Differential electrolytic etching of an alloy containing two or more phases at a controlled potential is possible only when each phase has a certain characteristic polarization curve. For effective differentiation of the phases, it is important that the difference in corrosion rates of the phase under study and of the other phases present be as large as possible at the chosen potential. Cihal and Prazak (31) termed this difference the differentiation ratio, D, given by

\[ D_A = \frac{i_A}{i_B} \exp \left( \frac{E}{E} \right) \]  

(160)

where \( i_A \) and \( i_B \) are the values of current per unit area of the phases A and B at the potential E. The differentiation ratio is independent of the proportion of the two phases present. Mannerkoski (39) utilized the above relationship
Fig. 25. The Anodic Polarization Behavior of (1) High Purity Ferritic Alloy NV-1 and (2) High Purity Austenitic Alloy 53 in 1N H₂SO₄ at 25°C.
to determine the effect of partial decomposition of austenite on the anodic polarization curve for a hardened 13 percent chromium steel.

In the event that the microstructure of the metal examined is heterogeneous, the anodic polarization curve obtained is the sum of the curves of each single phase, and if the electrode potentials of the phases are different additional loops beside the original may appear. This principle may be applied to detect the presence of carbide precipitation at the grain boundaries of sensitized alloys. Figure 26 shows the characteristic polarization curves of annealed and sensitized Type 304 stainless steel. The second peak exhibited by the sensitized specimen is attributed to a decrease in chromium content in the grain boundary areas.

It seems that it is now possible to follow some of the changes in corrosion behavior resulting either from alterations in composition or heat treatment by a study of anodic polarization curves. Such an investigation could help to explain some of the apparent abnormalities found in the literature.

2. Composition dependence

The anodic polarization behavior of all experimental alloys was determined in dilute sulfuric acid solutions at 25°C and at a scanning rate of approximately 100 millivolts per minute. Sufficient time at open circuit was allotted for
Fig. 26. Effect of Heat Treatment on the Anodic Polarization Response of Type 304 Stainless Steel in 1N H₂SO₄ at 25°C. (80 mv/min) (1) Annealed (2) Sensitized.
each alloy to attain near steady-state conditions before the potential was altered. Current response was recorded automatically as the potential was changed linearly from the open circuit potential to a potential beyond which oxygen evolution appeared. The current density was calculated on the basis of geometric area from the current-potential curves at 20 millivolt intervals and the data transferred to semilogarithmic paper. Potential values on the abscissa were referred to the standard calomel electrode (SCE) in terms of the European sign convention. Duplicate experiments were conducted on each sample when it was necessary to confirm previous results. However, reproducibility was good and the majority of the polarization curves were determined only once.

The experimental results are presented in groups that most adequately show the effect of composition on anodic polarization behavior in the given environment. Groupings which represent Figures 27 through 32 are as follows:

- Figure 27. Fe, Fe-10Ni, Fe-20Ni, Ni,
- Figure 28. Fe, Fe-10Cr, Fe-20Cr, Cr,
- Figure 29. Fe-10Cr, Fe-10Cr-10Ni, Fe-10Cr-20Ni,
- Figure 30. Fe-10Ni, Fe-10Ni-10Cr, Fe-10Ni-20Cr,
- Figure 31. Fe-20Cr, Fe-20Cr-10Ni, Fe-20Cr-20 Ni, and
- Figure 32. Fe-20Ni, Fe-20Ni-10Cr, Fe-20Ni-20Cr.

The other set of curves, Figures 33 through 42, contrasts the effect of fourth-component additions on the polarization characteristics of an Fe-20Cr-15Ni alloy (Alloy 54). Additions of phosphorous, oxygen, platinum, silicon, carbon,
Fig. 27. The Effect of Nickel on the Anodic Behavior of Iron Alloys in 1N H₂SO₄ at 25°C. (1) Fe (2) Fe-10Ni (3) Fe-20Ni (4) Ni.
Fig. 28. Effect of Chromium on the Anodic Behavior of Iron Alloys in 1N H₂SO₄ at 25°C. (1) Fe (2) Fe-10Cr (3) Fe-20Cr (4) Cr.
Fig. 29. The Effect of Nickel on the Anodic Behavior of Fe-10Cr Alloys in 1N H₂SO₄ at 25°C. (1) Fe-10Cr (2) Fe-10Cr-10Ni (3) Fe-10Cr-20Ni.
Fig. 30. The Effect of Chromium on the Anodic Behavior of Fe-10Ni Alloys in 1N H$_2$SO$_4$ at 25°C. (1) Fe-10Ni (2) Fe-10Ni-10Cr (3) Fe-10Ni-20Cr.
Fig. 31. The Effect of Nickel on the Anodic Behavior of Fe-20Cr Alloys in 1N H₂SO₄ at 25°C. (1) Fe-20Cr (2) Fe-20Cr-10Ni (3) Fe-20Cr-20Ni.
Fig. 32. The Effect of Chromium on the Anodic Behavior of Fe-20Ni Alloys in 1N H2SO4 at 25°C. (1) Fe-20Ni (2) Fe-20Ni-10Cr (3) Fe-20Ni-20Cr.
Fig. 33. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-18.77Cr-15.10Ni) and (2) Alloy 54-0.054P in 1N HgSO₄ at 25°C.
Fig. 34. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-18.77Cr-15.10Ni) and (2) Alloy 54-0.029 O in 1N H₂SO₄ at 25°C.
Fig. 35. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-18.77Cr-15.10Ni) and (2) Alloy 54-5.10Pt in 1N H₂SO₄ at 25°C.
Fig. 36. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-18.77Cr-15.10Ni) and (2) Alloy 54-0.76Si in 1N H₂SO₄ at 25°C.
Fig. 37. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-18.77Cr-15.10Ni) and (2) Alloy 54-0.15C in 1N H$_2$SO$_4$ at 25°C.
Fig. 38. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-17.77Cr-15.10Ni) and (2) Alloy 54-1.71Cu in 1N H₂SO₄ at 25°C.
Fig. 39. The Anodic Polarization Behavior of (1) Alloy 54 \( \text{(Fe-19.77\%Cr-15.10\%Ni)} \) and (2) Alloy 54-2.65Mo in 1N \( H_2SO_4 \) at 25°C.
Fig. 41. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-18.77Cr-15.10Ni) and (2) Alloy 54-0.058S in 1N H$_2$SO$_4$ at 25°C.
Fig. 42. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-18.77Cr-15.10Ni) and (2) Alloy 54-0.025N in 1N H₂SO₄ at 25°C.
copper, molybdenum, manganese, sulfur, and nitrogen are included. In addition, a comparison between Alloy 54 and Commercial Type 309 stainless steel is indicated in Figure 43.

A predominant trend in the general shape of the curves with respect to composition is self evident. Changes in open circuit potential, critical current density, passive current density, and transpassive behavior are discussed in detail later.

3. **Effect of pH**

A change in the hydrogen ion concentration in dilute solutions of sulfuric acid has a pronounced effect on the polarization characteristics of pure iron, pure chromium, and pure nickel electrodes as shown in Figures 44 through 46. Although the significant regions of the curves are apparent in each case it is observed that the critical values are displaced somewhat on the current and potential axis as a function of the composition of the electrolyte. The shift is more pronounced for the case of chromium and nickel than it is for iron. A change in the corrosion potential to more negative values with increasing pH is evident in each case.

C. **Corrosion potential**

The electrochemical theory states that metals corrode due to the formation of local cells on their surfaces. These cells consist of anodic areas, where oxidation occurs, and
Fig. 43. The Anodic Polarization Behavior of (1) Alloy 54 (Fe-18.77Cr-15.10Ni) and (2) Type 309 Stainless Steel in 1N H₂SO₄ at 25°C.
Fig. 44. Effect of Hydrogen Ion Activity on the Anodic Behavior of Iron. (1) 1.0 N H$_2$SO$_4$ (2) 0.1 N H$_2$SO$_4$
(3) 0.01 N H$_2$SO$_4$ (4) 0.001 N H$_2$SO$_4$. 
Fig. 45. Effect of Hydrogen Ion Activity on the Anodic behavior of Chromium. (1) 1.0N H₂SO₄  (2) 0.1N H₂SO₄ 
(3) 0.1N H₂SO₄  (4) 0.001N H₂SO₄.
Fig. 46. Effect of Hydrogen Ion Activity on the Anodic Behavior of Nickel. (1) 1.0N H₂SO₄  (2) 0.1N H₂SO₄
(3) 0.01N H₂SO₄  (4) 0.001N H₂SO₄.
cathodic areas, where there is an equivalent reduction. The driving force which enables the reactions to proceed is provided by the difference in potential of the local anodic and cathodic cells. According to Faraday's law the rate of corrosion is determined by the quantity of electricity which is carried by electrons through the metal. The current is passed through the solution by electrolytic transference to complete the circuit. Since the reactions occurring are electrochemical, they are associated with a definite potential consisting of the sum of the reversible or open-circuit potentials, for the given reactions and a polarization term which results from the flow of current. The open-circuit potential of the less negative or anodic process is the equilibrium potential calculated from thermodynamic principles. The potential of the cathodic process is dependent upon the characteristics of the environment. In an acid solution, the open-circuit potential of the cathodic reaction, i.e., the reduction of hydrogen ions, is given by the potential of a reversible hydrogen electrode. A flow of current is established as a result of a difference in potential between the local corrosion cells. Consequently, the potential of the anodic reaction shifts in the cathodic direction and the potential of the cathodic reaction becomes more anodic. Due to polarization effects, the resultant potential of the corroding metal lies somewhere between the
equilibrium values of the two reactions and is determined by the intersection of the anodic and cathodic polarization curves. The local anodic current at this point is equivalent to the corrosion rate in accordance with Faraday's law. Since the potential difference can never equal zero the reactions are polarized sufficiently to drive the corrosion current through the total resistance of the circuit (40).

When the local cells on the corroding electrode are subjected to an applied current the resultant anodic and cathodic polarization curves may be measured. The corrosion current and thus the corrosion rate is determined by extrapolating the linear portion of either or both polarization curves to the corrosion potential. It must be assumed, however, that the application of an external current does not alter the mechanisms of the electrochemical processes which occur during local-cell corrosion. This technique was employed by Stern (41) to interpret corrosion processes and to measure corrosion rates on metal surfaces.

Stern (13) has developed a graphical technique in which cathodic polarization behavior can be used to estimate the corrosion rate. The method, based on the relation between hydrogen overvoltage and current density, at current densities low enough to avoid concentration polarization, is expressed as

\[
\eta_a = \beta \log \frac{1}{i} \quad (161)
\]
where \( \eta_a \) is the hydrogen (activation) overvoltage or potential measured against a hydrogen electrode in the same solution, \( \beta \) is a constant equal to the slope of the Tafel region, \( i \) is the total cathodic current density, and \( i_0 \) is the exchange current density or the current equal to the equilibrium rate of hydrogen reduction at the reversible hydrogen potential. The mechanics leading to the development of the above relationship have previously been given. In the case of a corroding metal it is apparent that the total cathodic current density, \( i \), in equation (161) is replaced by the sum of two separate terms—

1. \( i_{EC} \), the externally applied cathodic current density, and

2. \( i_{LA} \), the local action current density.

Stern concluded that the two are obviously not independent since the principle of cathodic protection is based on the reduction of \( i_{LA} \) with an increase of \( i_{EC} \). Thus, the above equation may be written in a more general form

\[
\eta_a = \beta \log \frac{i_{EC} + i_{LA}}{i_0}
\]  

(162)

In accordance with observation, equation (162) predicts that the potential remains relatively constant until the magnitude of the externally applied current is equivalent to that of the local action current. When the former is equal to zero, i.e., with no external applied current, \( \eta_a \)
equals the corrosion potential, $E_{\text{corr}}$, on the hydrogen overvoltage scale, and $i_{\text{LA}}$ equals the corrosion current, $i_{\text{corr}}$, hence

$$E_{\text{corr}} = \beta \log \frac{i_{\text{corr}}}{i_o}$$

This equation may be used to calculate the corrosion current if $\beta$, the slope of the cathodic polarization curve in the Tafel region, the corrosion potential, and the exchange current, $i_o$, are known. The latter value is determined graphically by extrapolating the Tafel region to the reversible hydrogen potential.

Equation (163) is valid only if the total area of the specimen on which the cathodic reaction proceeds is functioning as the cathode. When the cathodic area is somewhat less than this, the estimated corrosion rate tends to be high by a factor determined by the actual cathode-to-anode area ratio. Stern (13) obtained very good agreement between calculated and measured corrosion rates for iron in deaerated acid solutions because his data indicated the existence of a very high cathode-to-anode area ratio. This fact was later observed by Uhlig (38) who concluded that the fraction of total area representing the anode in the corrosion reaction is equal to about 0.006. Thus, at any time, the total anodic area is probably much less than the cathodic area, even
though anodes and cathodes interchange relative positions as the reactions occur.

1. Composition dependence

The Tafel slope of the cathodic polarization curve, the exchange current, and the corrosion potential for each of the experimental alloys are given in Tables 9, 10, and 11. It was necessary to measure the corrosion potential before and after cathodic polarization. A sufficient time was allotted for all specimens to attain equilibrium conditions prior to the determination of polarization characteristics. Time potential measurements revealed that the open-circuit potential varied in a parabolic manner with time. Usually, 30 to 120 minutes were required for each reading.

The addition of nickel to iron and to iron-chromium alloys displaces the corrosion potential to more noble values and simultaneously reduces the magnitude of the corrosion current by increasing the overvoltage of the anodic dissolution reaction. In a completely ferritic matrix, chromium shifts the open-circuit potential in the negative direction and increases the rate of corrosion of iron-rich, iron-chromium alloys in sulfuric acid. This effect is predicted from the theory of mixed potentials in which the corrosion behavior of single phase alloys is predominately under anodic control. The effect of chromium is less predictable in alloys which exhibit a two-phase structure.
<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Hydrogen Electrode Potential, mv (SCE)</th>
<th>Corrosion Potential, mv (SCE)</th>
<th>Hydrogen Exchange Current Density, ma/cm²</th>
<th>Corrosion Current Density, ma/cm²</th>
<th>Total Slope</th>
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**TABLE 9**

CHARACTERISTIC (CATHODIC) POLARIZATION PROPERTIES OF EXPERIMENTAL ALLOYS IN SULFURIC ACID ACID SOLUTIONS AT 25°C
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<tr>
<th>Alloy Composition</th>
<th>Hydrogen Electrode Potential, mv (SCE)</th>
<th>Corrosion Potential, mv (SCE)</th>
<th>Hydrogen Exchange Current Density, ma/cm²</th>
<th>Corrosion Current Density, ma/cm²</th>
<th>Total Slope</th>
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<tr>
<td>54-N</td>
<td>-287</td>
<td>-397</td>
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<td>0.523</td>
<td>0.0726</td>
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<tr>
<td>309</td>
<td>-288</td>
<td>-299</td>
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</tr>
</tbody>
</table>
### TABLE 11
CHARACTERISTIC (CATHODIC) POLARIZATION PROPERTIES OF IRON, CHROMIUM AND NICKEL IN SULFURIC ACID SOLUTIONS AT 25°C

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Hydrogen Electrode Potential, mv (SCE)</th>
<th>Corrosion Potential, mv (SCE)</th>
<th>Hydrogen Exchange Current Density, ma/cm²</th>
<th>Corrosion Current Density, ma/cm²</th>
<th>Total Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>-295</td>
<td>-516</td>
<td>0.0401</td>
<td>2.37</td>
<td>0.125</td>
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<tr>
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<tr>
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</tr>
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<td>Nickel</td>
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<td>0.560</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>-352</td>
<td>-351</td>
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<td>0.0943</td>
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<td>-388</td>
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<td>0.0685</td>
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<tr>
<td></td>
<td>-422</td>
<td>-418</td>
<td>0.0315</td>
<td>0.0292</td>
<td>0.139</td>
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</tr>
</tbody>
</table>

The behavior of two-phase alloys is more complicated, nevertheless a qualitative analysis can be given to explain the shift in corrosion potential with changing composition. The Tafel slope for hydrogen evolution is less for chromium than for iron and nickel in sulfuric acid. Since a greater concentration of chromium exists in the ferrite phase of a duplex alloy it is assumed that hydrogen evolution occurs at a faster rate on this than on the austenite phase. Galvanic experiments indicate that ferrite is attacked anodically in preference to the austenite phase which
contains less chromium. Thus, as the chromium content in iron-nickel alloys is increased, the corrosion potential becomes more noble because of an increasing percentage of austenite which polarizes the hydrogen reaction. As the ratio of austenite to ferrite increases, the rate of corrosion decreases, until at some composition the metal becomes completely austenitic. With increasing chromium content the open-circuit potential decreases and the corrosion current increases in accordance with the more electrochemically active behavior of chromium.

Additions of phosphorous, oxygen, silicon, sulfur, and nitrogen have little or no effect on the corrosion potential of an Fe-20Cr-15Ni alloy in 1N H₂SO₄ at 25°C, however platinum, carbon, copper, molybdenum, and manganese induce passivity in this environment.

2. Effect of pH

Metals which permit the rapid establishment of equilibrium between molecular hydrogen and hydrogen ions in solutions, thus

\[ \frac{1}{2} H_2(g) \rightleftharpoons \frac{1}{2} H_2(M) + H_2O \rightleftharpoons H_3O^+ + e^- \]  

(164)

are said to behave as reversible hydrogen electrodes. The general form of the equation for any electrode, reversible with respect to a single ion of valence n, is
\[ E = E^0 - \frac{RT}{nF} \ln a_i \]  
(165)

where \( a_i \) is the activity of the particular ionic species.

By converting the logarithm from Naperian to Briggsian and inserting the values of \( R \) (8.313 joules) and \( F \) (96,500 coulombs) into the above equation, the result at 25°C is

\[ E = E^0 - \frac{0.05915}{n} \log a_i \]  
(166)

For the reversible hydrogen electrode, \( a_i = a_{H^3O^+} \) and \( n = 1 \), consequently

\[ E = E^0 + 0.05915 \, \text{pH} \]  
(167)

Thus, the potential of an electrode which is reversible with respect to the concentration of hydrogen ions in solution is a linear function of the logarithm of the pH.

Corrosion potentials for pure iron, pure chromium, and pure nickel in dilute solutions of sulfuric acid are listed in Table 11. In addition, the pH dependence of the open-circuit potential of each electrode is presented in Figure 47. The slopes, \( \mathrm{d}E/\mathrm{d}(\text{pH}) \), were determined by the method of least squares.

In all probability, the shift in potential as a function of pH may be attributed to a very large cathode-to-anode area ratio which increases with decreasing pH in the vicinity of the corrosion potential (13). Another explanation offered by Stern and Roth (42) attributes the negative
Fig. 47. Effect of pH on the Corrosion Potential of Iron, Chromium, and Nickel in Hydrogen-saturated Solutions of Sulfuric Acid at 25°C.
shift in potential to the reduction of the exchange current for the metal/metal-ion reaction as the pH decreases. Tafel slopes for the anodic dissolution of iron based on the second method were found to be approximately 0.068 volts to 0.078 volts. Stern (13) later found that the experimental slope for the steady-state corrosion potential of iron in deaerated acidic NaCl over a pH range of 1 to 5 was 0.0559 volts. This agrees more favorably with the theoretical value of 0.05915 volts. At present, no experiment can distinguish between the two proposed mechanisms, but the explanation based on decreasing anode area appears to be the most promising.

D. Active-to-passive transition

One of the most important aspects of anodic polarization behavior is the conversion of a metal from the active to the passive state. It is frequently observed, with increasing potential, that the film-free area on the metal surface decreases exponentially at a greater rate than the exponential reduction of the magnitude of the anodic dissolution current. When the passivation potential is reached the anodic current density decreases exponentially to a very low value characteristic of the passive state. The mechanism of the reactions which contribute to the formation of a passivating film on metals is of basic interest in studying
the nature of passivity and corrosion control. A model presented by Mueller (43) is of special interest since good agreement of theory is shown by published data for iron, nickel, chromium, gold, and silver. It is based on the assumption that passivation of metals by oxides is caused by the reaction of hydroxyl ions with the metal surface. The principles and formulas, however, are applicable to the electrochemical passivation by other films. General relationships are developed which describe the density of the anodic dissolution current as a function of the pH and the potential difference between the metal and the electrolyte. For example, an equation is derived which covers the density of anodic dissolution current as a function of the potential including the active and passive states.

\[
1_c = 2i_{0.5} e^{\frac{\alpha a F}{RT} (E-E_{0.5})^2} \left(1 + \exp \frac{\alpha p F}{RT} (E-E_{0.5})\right) (168)
\]

where

\(1_c\) = anodic current density,

\(i_{0.5}\) = current density when surface is 50 per cent covered by protective film,

\(E_{0.5}\) = potential corresponding to \(i_{0.5}\),

\(1_p\) = passive current density,

\(\alpha a\) = symmetry factor of anodic reaction,

\(\alpha p\) = symmetry factor of passive film-forming reaction,

\(n_a\) = valency of anodic dissolution reaction, and

\(n_p\) = valency of passive film-forming reaction.
In semilogarithmic plotting the calculated curve assumes a very simple form, and in limited cases all the characteristic constants in the above equation can be calculated from experimental measurements. In the active state the second term in both the numerator and denominator is negligible and the resulting equation gives the straight line

\[
\frac{d\ln i_c}{dE} = \frac{\chi a^n F}{RT}
\]

which is an alternate form of the Tafel equation. For the conversion from the active to the passive state the second term in the numerator and the first term in the denominator become negligible, hence

\[
\frac{d\ln i_c}{dE} = \frac{(\chi a^n - \chi p^n) F}{RT}
\]

Similarly, in the passive range the first term of each numerator and denominator becomes small in comparison with the second term and

\[
i_c = i_p
\]

Mueller explained that the straight lines given by equations (169) and (170) cross at the coordinates 210.5 and E0.5 and the second and third straight lines cross at the coordinates ip and Ef.
The ratio $\frac{\gamma_{an}}{\gamma_{pn}}$ determines the form of the curve of the anodic dissolution current density. If the ratio is unity the curve forms a polarographic wave which is indicative of the formation of a region of constant current density. For example, such an area might be caused by a film of salt. When the ratio is equal to two, the curve is symmetrical and a negative slope is obtained for equation (170). For ratios greater than two, the current density in the range of the conversion from the active to the passive state decreases at a faster rate than it increases in the active range.

The above relationships adequately describe the general form of the experimental anodic polarization curves for a number of alloys in dilute solutions of sulfuric acid.

1. Tafel behavior

In general, at any electrode, two currents may be regarded as flowing in opposite directions. The net current is the difference between the opposing anodic and cathodic components. When equilibrium conditions are established, i.e., when the anodic and cathodic currents are in balance, the current flowing in each direction is known as the exchange current $I_0$. The corresponding current density $I_0/A$, where $A$ is the electrode area is designated $i_0$. If the potential of the electrode is shifted from equilibrium, for example in an anodic direction, the cathodic component
can be neglected. The departure of the potential from the equilibrium value is termed polarization. According to Evans (44), for normal metals, a small departure from equilibrium causes an appreciable flow of current, whereas for abnormal metals like iron and nickel, a considerable departure is necessary.

The net current density in the anodic direction, $i_a$, in the above case, is given with sufficient accuracy by the term

$$i_a = nFk_1 e^{\frac{\alpha nF(E+n\alpha)}{RT}}$$

which was previously derived. Similarly, the exchange current density is defined as

$$i_0 = nFk_1 e^{\frac{\alpha nFE}{RT}}$$

It follows that

$$\ln \left( \frac{i_a}{i_0} \right) = \frac{\alpha nF}{RT} \eta_a$$

or

$$\eta_a = 2.303 \frac{RT}{\alpha nF} \log \frac{i_a}{i_0} = b \log \frac{i_a}{i_0}$$

This equation is often written in the form

$$\eta_a = a + b \log i_a$$
where $a$ represents $-b \log \eta$; $a$ and $b$ are both constants independent of $\eta_a$. This is known as Tafel's equation and $b$ is called the Tafel slope. In general, the slope of the initial section of the anodic polarization curve for an ion of valence $n$ is $2.303RT/\eta nF$, and at ordinary temperatures becomes $0.05915/\eta n$ where $\eta$ lies between zero and unity. A similar treatment may be provided for the case when the net current flow is in the cathodic direction.

The magnitude of the range over which Tafel behavior exists is controlled by several factors. First, a lower limit of the linear range is established when the net current flow exceeds the influence of the opposing exchange current. Second, deviation from Tafel behavior occurs when the limited current is approached as a result of concentration polarization. The latter effect can be minimized, however, by vigorously stirring the solution. In addition, compensation should be made for ohmic overpotential which becomes appreciable at high current densities.

Tafel slopes reported in Tables 12, 13, and 14 were determined from anodic polarization curves of experimental alloys which demonstrated Tafel behavior over a sufficient range of current density.

2. Critical current density

When the potential of an electrode is increased in the anodic direction a net current flows due to the passage of
### TABLE 12

**CHARACTERISTIC (ANODIC) POLARIZATION PROPERTIES OF EXPERIMENTAL ALLOYS IN SULFURIC ACID SOLUTION AT 25°C**

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Hydrogen Electrode Potential, mv (SCE)</th>
<th>Corrosion Potential, mv (SCE)</th>
<th>Corrosion Current Density, ma/cm²</th>
<th>Total Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>-295</td>
<td>-505</td>
<td>2.37</td>
<td>0.0520</td>
</tr>
<tr>
<td>Fe-10Ni</td>
<td>-296</td>
<td>-428</td>
<td>1.63</td>
<td>0.0380</td>
</tr>
<tr>
<td>Fe-20Ni</td>
<td>-294</td>
<td>-387</td>
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<td>0.103</td>
</tr>
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<td>Ni</td>
<td>-295</td>
<td>-296</td>
<td>0.560</td>
<td>0.120</td>
</tr>
<tr>
<td>Fe-10Ni-10Cr</td>
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<td>-428</td>
<td>1.63</td>
<td>0.0380</td>
</tr>
<tr>
<td>Fe-10Ni-20Cr</td>
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<td>-424</td>
<td>1.55</td>
<td>0.0620</td>
</tr>
<tr>
<td>Fe-20Ni</td>
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<td>-387</td>
<td>0.963</td>
<td>0.103</td>
</tr>
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<td>Fe-20Ni-10Cr</td>
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<td>0.0940</td>
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<td>0.302</td>
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<td>Fe</td>
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<td>-505</td>
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<td>Cr</td>
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<td>9.17</td>
<td>0.0650</td>
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<td>-542</td>
<td>4.04</td>
<td>0.0500</td>
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<td>-342</td>
<td>0.563</td>
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<td>-567</td>
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<td>0.0280</td>
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<td>-424</td>
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<td>0.0620</td>
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<tr>
<td>Fe-20Cr-20Ni</td>
<td>-296</td>
<td>-362</td>
<td>0.302</td>
<td>0.0790</td>
</tr>
<tr>
<td>Alloy Composition</td>
<td>Hydrogen Electrode Potential, mv (SCE)</td>
<td>Corrosion Potential, mv (SCE)</td>
<td>Corrosion Current Density, ma/cm²</td>
<td>Total Slope</td>
</tr>
<tr>
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<td>54-Mo</td>
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<td>54-Mn</td>
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<td>0.0370</td>
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<td>Pure Material</td>
<td>Hydrogen Electrode Potential, mv (SCE)</td>
<td>Corrosion Potential, mv (SCE)</td>
<td>Corrosion Current Density, ma/cm²</td>
<td>Total Slopes</td>
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<td>---------------</td>
<td>--------------------------------------</td>
<td>-------------------------------</td>
<td>----------------------------------</td>
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<td>-0.577</td>
<td>0.615</td>
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<td>0.268</td>
<td>0.0390</td>
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<td>-0.420</td>
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<td>0.0350</td>
</tr>
<tr>
<td>Chromium</td>
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<td>-0.697</td>
<td>9.17</td>
<td>0.0650</td>
</tr>
<tr>
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<td>-0.761</td>
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<td>-0.391</td>
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<td>0.0470</td>
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<td>-0.296</td>
<td>0.560</td>
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</tr>
<tr>
<td></td>
<td>-0.352</td>
<td>-0.351</td>
<td>0.0943</td>
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<td>-0.390</td>
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<td>0.187</td>
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<tr>
<td></td>
<td>-0.422</td>
<td>-0.421</td>
<td>0.0292</td>
<td>0.153</td>
</tr>
</tbody>
</table>

Ions into solution. Initially, the current flow is a linear function of potential and the dissolution reaction is said to be under activation control. At a sufficiently high potential the limiting current density is approached and the concentration of metal ions in the vicinity of the electrode increases. The current response deviates from linearity at this point due to the effects of concentration polarization. Supersaturation of the electrolyte in the vicinity of the electrode results in the formation of a metal compound. Anodic passivation occurs very quickly in this potential
range if the metal compound formed by the emerging cations is thermodynamically stable. Consequently, the flow of metal cations from the metal surface is greatly diminished and the onset of passivity is indicated by a rapid fall in current density. The maximum current density recorded in the active region of the polarization diagram is designated $i_c$, the critical current density for passivation. At this point conditions are established which make possible the formation of a stable protective film on the exposed surface of the anode.

The critical current density for passivation and the potential associated with each current density maximum was determined for most alloys and environments used in this experimental program. These values are presented in Tables 15, 16, and 17. The study was not complete because the critical current density of alloys which exhibited self-passivity in the chosen environment could not be accurately determined.

As pointed out by Hoar (45), the formation and stability of the passive film depends largely upon the degree of solubility of the metal compound formed by the emerging cations and the solution anions or solvent. When a sparingly soluble product is formed anodic passivation may occur very quickly. On the other hand, when the initial anodic product is freely soluble a much greater passage of
## TABLE 15

**CRITICAL CURRENT DENSITY FOR PASSIVATION OF EXPERIMENTAL ALLOYS IN SULFURIC ACID SOLUTIONS AT 25°C**

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>pH of Solution</th>
<th>Critical Current Density, $I_c$, mA/cm²</th>
<th>Potential at Current Maximum, mv (SCE)</th>
</tr>
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<tbody>
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<td>Fe</td>
<td>0.90</td>
<td>764.61</td>
<td>-333</td>
</tr>
<tr>
<td>Fe-1ONi</td>
<td>0.91</td>
<td>723.60</td>
<td>-220</td>
</tr>
<tr>
<td>Fe-2ONi</td>
<td>0.89</td>
<td>619.36</td>
<td>-200</td>
</tr>
<tr>
<td>Ni</td>
<td>0.90</td>
<td>5.19</td>
<td>+60</td>
</tr>
<tr>
<td>Fe-1ONi</td>
<td>0.91</td>
<td>723.60</td>
<td>-220</td>
</tr>
<tr>
<td>Fe-1ONi-10Cr</td>
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<td>34.82</td>
<td>-326</td>
</tr>
<tr>
<td>Fe-1ONi-20Cr</td>
<td>0.89</td>
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<td>-335</td>
</tr>
<tr>
<td>Fe-2ONi</td>
<td>0.89</td>
<td>619.36</td>
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<td>Fe-2ONi-20Cr</td>
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<td>1.33</td>
<td>-282</td>
</tr>
<tr>
<td>Fe</td>
<td>0.90</td>
<td>764.61</td>
<td>-333</td>
</tr>
<tr>
<td>Fe-10Cr</td>
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<td>-436</td>
</tr>
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<td>Fe-20Cr</td>
<td>0.90</td>
<td>106.62</td>
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</tr>
<tr>
<td>Cr</td>
<td>0.89</td>
<td>8.11</td>
<td>-620</td>
</tr>
<tr>
<td>Fe-10Cr</td>
<td>0.72</td>
<td>149.84</td>
<td>-436</td>
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<tr>
<td>Fe-10Cr-1ONi</td>
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<td>106.62</td>
<td>-486</td>
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<td>0.90</td>
<td>1.33</td>
<td>-282</td>
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</table>
TABLE 16
CRITICAL CURRENT DENSITY FOR PASSIVATION OF FOURTH COMPONENT ALLOYS IN SULFURIC ACID SOLUTIONS AT 25°C

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>pH of Solution</th>
<th>Critical Current Density, I_C, ma/cm²</th>
<th>Potential at Current Maximum, mv (SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>0.74</td>
<td>6.01</td>
<td>-310</td>
</tr>
<tr>
<td>54-P</td>
<td>0.78</td>
<td>0.25</td>
<td>-354</td>
</tr>
<tr>
<td>54-O</td>
<td>0.75</td>
<td>0.87</td>
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</tr>
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<td>54-Pt</td>
<td>0.85</td>
<td>0.53</td>
<td>-286</td>
</tr>
<tr>
<td>54-Si</td>
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<td>54-C</td>
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<tr>
<td>309</td>
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<td>0.03</td>
<td>-230</td>
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</tbody>
</table>
TABLE 17
CRITICAL CURRENT DENSITY FOR PASSIVATION OF IRON, CHROMIUM AND NICKEL IN SULFURIC ACID SOLUTIONS AT 25°C

<table>
<thead>
<tr>
<th>Alloy Material</th>
<th>pH of Solution</th>
<th>Critical Current Density, $I_c$, ma/cm²</th>
<th>Potential at Current Maximum, mv (SCE)</th>
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<td>-410</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0.89</td>
<td>8.11</td>
<td>-620</td>
</tr>
<tr>
<td></td>
<td>1.86</td>
<td>1.90</td>
<td>-654</td>
</tr>
<tr>
<td></td>
<td>2.52</td>
<td>1.65</td>
<td>-697</td>
</tr>
<tr>
<td></td>
<td>2.70</td>
<td>1.27</td>
<td>-711</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>5.19</td>
<td>+ 60</td>
</tr>
<tr>
<td></td>
<td>1.86</td>
<td>1.07</td>
<td>+ 33</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>0.51</td>
<td>+ 23</td>
</tr>
<tr>
<td></td>
<td>3.04</td>
<td>0.34</td>
<td>- 19</td>
</tr>
</tbody>
</table>

current is required before passivation is set up. In the latter case, the onset of passivity may be attributed to the precipitation of an otherwise soluble corrosion product as a result of supersaturation, or to the attainment of a critical pH immediately adjacent to the anode. These conditions favor the formation of a compact solid film, such as an oxide or hydroxide, which substantially reduces the rate of anodic dissolution. The formation of an insoluble metal compound is usually identified by a corresponding current or potential arrest in the anodic polarization diagram. In potentiostatic experiments, the potential differs from the
value calculated from thermodynamics data by a few millivolts in the positive direction during passivation and by a few millivolts in the negative direction during activation. The nearly reversible behavior is good evidence for the formation of known compounds associated with these potential values. Additional evidence for the formation of an oxide, hydroxide, or metal salt is the pH dependence of the potential in question. The passivation potential of a number of metals obeys the relation

\[ E_p = E_p^0 - 0.05915 \text{ pH} \quad (177) \]

where \( E_p^0 \) is the standard value of \( E_p \) at \( \text{pH} = 0 \). Flade (46) identified the passivation potential of iron in this manner

\[ E_p = 0.340 - 0.05915 \text{ pH (SCE)} \quad (178) \]

which suggests that either an oxide higher than \( \text{Fe}_2\text{O}_3 \), or adsorbed oxygen, is responsible for the passivation of iron.

**Iron**

Recent studies concerning the passivation of iron in sulfuric acid confirm the belief originally held by Muller (47) that ferrous sulfate is the first to precipitate. The actual passivating film, however, is an oxide which forms in the pores of the ferrous sulfate layer and then spreads laterally over the surface of the anode. These events, as
described by Evans (44), are clearly evident in the appended anodic polarization diagram.

It is shown in the initial section of the curve that the current increases to a maximum and then falls abruptly to a lower value as the potential is moved in the positive direction. At the maximum point the liquid next to the electrode becomes so supersaturated with ferrous sulfate that a crystalline layer forms on the surface. Since nucleation energy is required, there is always a lag in the appearance of the crystalline phase. The maximum and minimum values are characteristic of the rate of increase of the applied potential. When the potential is raised very rapidly the value of the critical current density increases and the drop is more severe, owing to a greater degree of supersaturation. Beyond this point the current rises slowly and then tapers off to a relatively constant value, at which time the production of ferrous sulfate exactly balances dissolution by the liquid. The latter depends on convection and diffusion but not on potential. The rate of metal dissolution at the base of pores in the crystalline layer, as indicated by the current in the horizontal section, is sufficient to replenish the loss due to film dissolution.

Violent current oscillations appear at the end of the horizontal section. This unusual behavior involves the formation and dissolution of a solid oxide film at the base of
pores or cracks in the crystalline layer which is dependent on the acidity of the environment. In all probability, the pH of the solution contained in these perforations is much higher than it is in the bulk of the solution. As a result the current density drops, as indicated in the polarization diagram, to a very low value due to oxide formation. When this happens ferrous sulfate is dissolved by the electrolyte without subsequent reformation. The iron soon becomes exposed to acid of nearly full strength and immediately the oxide dissolves. Consequently, ferrous sulfate is again formed due to the large surge of current from the bare electrode. This process is continually repeated until the oxide film becomes stable at a more positive potential.

Additional information concerning these occurrences are found in the reported experimental data. For instance, the anodic polarization curves indicate that the critical current density and the potential at that point are nearly independent of hydrogen ion concentration. Furthermore, fluctuations which occur during the active-to-passive transition are reduced as the acidity of the electrolyte decreases and, at the same time, the passivation potential is displaced in the negative direction. Since the sulfate ion concentration is held constant in all solutions no conclusions can be drawn concerning its role in the passivation of iron. It should be noted, however, that this is the
only constituent in the electrolyte that remains unchanged. Serra and Feliu (48) concluded that the sulfate ion is unimportant and that the accumulation of ferrous ions is the dominating factor. This may very well be true since the critical current density occurs at the same potential in all solutions.

Chromium

The mechanism offered by Roberts and Shutt (49) for the passivity of chromium agrees favorably with the experimental results of this program. They explained that the concentration of chromous ions is increased when the potential is displaced in the positive direction, while the hydrogen ion concentration is decreased by migration away from the surface of the electrode. The movement of ions increases with current density but the rate of diffusion, which opposes the rate of migration, remains practically unaltered. When the limiting current density is approached, the local concentration of hydrogen ions becomes sufficiently low to permit the discharge of either sulfate or hydroxyl ions. The latter reaction predominates in solutions of low acidity. Since no soluble chromous or chromic compounds can be formed with increasing potential, the proportion of hydroxyl ions adsorbed and discharged upon the surface of the electrode increases in proportion to the current density.
Primary contact of the metal lattice with oxygen-containing ions results in the direct formation of an oxide or hydroxide film which gradually covers the chromium surface. This film, as pointed out by the above authors, may not necessarily correspond to any known compound of the metal, but should be regarded as a Langmuir film, "continuous with the chromium lattice and electromotively active in the sense that its potential depends on the degree of oxidation."

Since the limiting current density represents the current strength at which electrical migration just overcomes diffusion, the critical current density for passivation should increase with increasing acidity of the electrolyte. General agreement between the experimental results and the mechanism proposed above is considered satisfactory.

**Nickel**

The first critical observations on the behavior of nickel in sulfuric acid were made by Muller (47) and by Hedges (50). Recent studies by others have confirmed some of Muller's early work. In general, Turner (51) found that the accumulation of metal ions in the vicinity of the electrode resulted in the precipitation of a basic nickel sulfate. Hoar (45) suggested that an increase in pH may also be important in this case is indicated in Figure 45 which shows that passivation sets in much sooner in solutions of low acidity. In addition, Landsburg and Höllnagel (52)
found that pre-saturation of 0.2N H$_2$SO$_4$ with 3.96N NiSO$_4$ only moderately decreased the induction period, whereas an addition of 0.2N Na$_2$SO$_4$ to 0.02N H$_2$SO$_4$ greatly increased the passivation time. Apparently, in solutions of much greater ionic strength, the migration of hydrogen ions away from the anode is slowed down. These experiments strongly suggest that pH as well as the concentration of nickel ions at the anode surface are both important for the onset of passivation.

In solutions of low acidity a tendency to form nickel hydroxide exists as indicated by the deflections in the anodic polarization diagrams. When the potential is increased in the positive direction the concentration of negatively charged ions in the anolyte increases due to the migration of hydrogen ions away from the surface of the electrode. The anions available for discharge are sulfate ions, and at low concentrations of acid, hydroxyl ions. If a relatively high concentration of nickel ions is one of the criteria for passivity, as suggested above, then nickel sulfate does not precipitate until a much higher current density is attained. Thus, at low potentials both the hydroxyl and sulfate ions remain adsorbed on the surface of the anode. The number of hydroxyl ions adsorbed increases with decreasing pH. In solutions of intermediate acidity the hydroxide phase is not stable and the current density continues to
rise until nickel sulfate is formed. The deflection in the anodic polarization diagram is most pronounced in the electrolyte containing 0.001N H$_2$SO$_4$. In solutions of pH $\geq 7.4$, the hydroxide becomes stable and the onset of passivation occurs at more negative potentials.

**Iron-chromium-nickel alloys**

The influence of alloying elements on the polarization characteristics of iron-base alloys is difficult to interpret, especially in the case of multi-phase alloys where structural constituents may be important. Both factors are known to affect the kinetics of anodic and cathodic reactions which control the rate of corrosion processes in aqueous environments. Consequently, it is only possible to relate significant trends which alter the electrochemical properties of alloys in the active and passive states.

Prazak and Barton (53) observed that at least three cases must be considered and alloying elements influence the behavior differently in each case. The cases are—

1. The active state where no insoluble products are formed,

2. The active state where insoluble products are formed, and

3. The passive state.

In the first case the alloying elements influence the thermodynamic properties of the metal, whereas in the second and third cases, alloying changes the properties of
the corrosion products formed. According to the authors, the effect of alloying elements on the latter is much more diverse.

The addition of chromium to iron progressively lowers the critical current density and shifts the active range of the anodic polarization curve in the negative direction. It also reduces the violent fluctuations which are characteristic of the behavior of iron in dilute solutions of sulfuric acid. In addition, chromium effectively reduces the active corrosion of iron-nickel base-alloys by narrowing the active region and by displacing the passivation potential to more negative values. The addition of an electrochemically active metal like chromium is beneficial because it decreases the passivation potential, which makes it possible to passivate the alloy, even in a solution with weak oxidizing properties.

Olivier (54) observed that far less primary ferrous sulfate is formed on iron-chromium alloys, before passivation, than is formed on pure iron. Furthermore, when the chromium content exceeds about 6.7 per cent the amount of precipitated primary sulfate formed is negligible. The shift of the passivation potential to more negative values is, therefore, attributed to the prior formation of chromic oxide. In contrast with iron, the deciding factor for the onset of passivation in iron-chromium alloys is pH and not
the accumulation of cations nor the amount of primary sulfate which is formed.

The addition of nickel to pure iron results in a slight decrease in the critical current density and a shift of potential in the positive direction. A similar response is observed for iron-chromium materials alloyed with nickel. The displacement of the anodic polarization curves is attributed to the increased electrochemical nobility of the experimental alloys. This effect is predicted by Prazak and Barton (53) and is observed to follow the rules: "If a pure metal A is alloyed with a component B which is electrochemically nobler than A the anodic overpotential of the alloy is increased compared to that of A." When corrosion proceeds with hydrogen depolarization, as in the examples given above, the increasing electrochemical nobility of the alloys, with increasing nickel content, is followed by a significant reduction in the rate of dissolution.

Since the influence of nickel is apparent in the polarization diagrams the mechanism which controls the passivation of iron-nickel alloys is of interest here. It appears that the concentration of cations in the anolyte remains the dominant factor in the passivation of low nickel alloys. A reduction in the periodic fluctuations characteristic of the behavior of pure iron in the active-to-passive transition range suggests the formation of a basic nickel
salt in addition to the precipitation of a crystalline layer of ferrous sulfate. The relatively insoluble nickel sulfate apparently reduces the dissolution current which is required to continually renew the soluble ferrous sulfate inherent in the reaction mechanism of iron. This conclusion is substantiated by Economy, Speiser, Beck, and Fontana (55) who observed that the colors of the films formed in the active range change from gray-black for high iron alloys, to greenish black for a 50Fe-50Ni alloy, to light green for a pure nickel electrode. The light green color is characteristic of the basic nickel sulfate, NiSO₄ • 7H₂O.

The effects of fourth-component additions on the electrochemical behavior of an Fe-20Cr-15Ni alloy in 1N H₂SO₄ are indicated in Table 16 and in the corresponding polarization diagrams. Phosphorous, oxygen, silicon, sulfur, and nitrogen in small quantities do not alter the corrosion potential of the base-alloy, whereas additions of platinum, carbon, copper, molybdenum, and manganese induce passivity under the given environmental conditions. Phosphorous is the only element which displaces the active region of the polarization curve in the positive direction. The critical current density is highest in alloys containing silicon, sulfur, and nitrogen and lowest in alloys containing phosphorous and oxygen. In a similar study Shaw and Edwards (56) reported that both molybdenum and titanium in
commercial alloys lowers the critical current density, whereas niobium increases the rate of corrosion slightly in the active state.

The dissolution characteristics of a metal depend to a great extent on the kinetics of the electron-transfer reactions proceeding on its surface. Principles concerning the perfection of the crystal lattice of surface films, as discussed in theories of gaseous oxidation, are often valid for dissolution reactions in aqueous media at ambient temperatures (44). In an acid environment, containing little or no oxygen, the metal is under mixed control and the corrosion rate is determined by both the anodic polarization characteristics and the hydrogen overvoltage behavior of the material.

Factors which affect the final corrosion rate of metals are complex but can often be resolved into distinct shifts and changes in local cell polarization diagrams. In this manner, Hoar and Havenhand (57) reported that the most important factor in determining corrosion rates of various metals and alloys in acid environments is local anodic polarization. Stern (58) observed, however, that this is important but not always true. He pointed out that activation polarization of the anodic reaction depends on whether dissolution occurs at grain boundaries, at specific crystallographic planes, or at various surface imperfections.
Cathodic polarization, on the other hand, depends on metal structure and composition as well as on impurities and depolarizers in solution.

Using the polarization curve technique and considering both reactions Stern was able to exploit the effect of various alloying elements on the dissolution kinetics of iron in acid environments. For example, he found that—

1. Phosphorous alone increases the exchange current,

2. Sulfur functions by decreasing the Tafel slope (by changing the local anodic polarization characteristics, by changing the anode to cathode area ratio), and

3. Copper eliminates the detrimental effect of sulfur by lowering the exchange current.

Greene, Bishop and Stern (59) using a similar technique, observed that noble metals accumulate on an alloy surface during dissolution of the matrix metal and in most cases, surface enrichment increases the cathodic exchange current density and decreases the critical anodic current density. Both these effects enhance the passivating tendency of alloys containing noble metal additions. They verified these effects by alloying chromium with small amounts of various noble metals and markedly improving its corrosion resistance in sulfuric acid.

E. Phenomenon of passivity

At potentials more positive than the passivation potential the metal transforms to the passive state.
Passivity is attributed to the formation of a relatively stable protective film on the exposed surface of the electrode. The film is continually undergoing dissolution and repair as indicated by the small but significant corrosion current, $I_p$, called the passive current density. The magnitude of the corrosion current of the experimental materials and the potential range over which passivity exists is indicated in Tables 18, 19, and 20.

These data are of utmost importance in systems employing anodic protection as a means of corrosion control. From this standpoint, it is advantageous that the passivation area be as wide as possible so that the material can remain passive under more varied conditions. In addition, the passive current density should be low because in the event there is a shortage of the passivating agent, the rate of destruction of the passive film will be lessened.

Since the current flow from passivated anodes occurs at potentials below those required for alternative anodic reactions, it is concluded that the current through the film must be ionic. This transport of matter, according to Hoar (45), must lead either to some degree of film growth or be accompanied by external film dissolution. Vetter (60) pointed out, however, that ionic flow through oxide lattices at normal temperatures usually requires high electrical fields and in the potential range considered, it is unlikely
<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>pH of Solution</th>
<th>Passive Current Density $I_p$, ma/cm²</th>
<th>Passive Potential Range, mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.90</td>
<td>0.0468</td>
<td>+400 / +1280</td>
</tr>
<tr>
<td>Fe-10Ni</td>
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<td>0.0876</td>
<td>+400 / +1440</td>
</tr>
<tr>
<td>Fe-20Ni</td>
<td>0.89</td>
<td>0.0958</td>
<td>+340 / +1260</td>
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<td>pH of Solution</td>
<td>Passive Current Density $I_p$, ma/cm²</td>
<td>Passive Potential Range, mv</td>
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<td>± 0 / +860</td>
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<td>Passive Potential Range, mv</td>
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<td>----------------</td>
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<td>-----------------------------</td>
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<td>+340 / +1400</td>
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<td>2.52</td>
<td>0.1725</td>
<td>+300 / +1300</td>
</tr>
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<td></td>
<td>3.01</td>
<td>0.1899</td>
<td>+260 / +1200</td>
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<tr>
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<td>-380 / +4880</td>
</tr>
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<td>2.52</td>
<td>0.0016</td>
<td>-560 / +820</td>
</tr>
<tr>
<td></td>
<td>2.70</td>
<td>0.0000</td>
<td>-600 / +780</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.90</td>
<td>0.2547</td>
<td>+320 / +540</td>
</tr>
<tr>
<td></td>
<td>1.86</td>
<td>0.0976</td>
<td>+320 / +1080</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>0.0927</td>
<td>+400 / +880</td>
</tr>
<tr>
<td></td>
<td>3.04</td>
<td>0.02278</td>
<td>+200 / +980</td>
</tr>
</tbody>
</table>

that film growth will exceed a certain thickness. Beyond this point current flow must be associated with film dissolution. The final thickness of the film depends on its specific electrical properties and on the potential range over which it exists.

Iron

The passivation mechanism of iron has been in doubt for many years. Some maintain that the film is an adsorbed oxygen monolayer while others hold that it is a three-dimensional oxide film. Still others suggested that both
adsorbed monolayers and solid films play a part in the passivity of iron. In the latter case, oxygen is thought to be adsorbed first and then converted to an oxide by the incorporation of a metal ion. Results from kinetic studies can often be interpreted in terms of either theory. For example, Hoar (45) pointed out that the amount of molecules or atomic oxygen required to form a close-packed adsorbed monolayer is sufficient to form a solid oxide film some two monolayers thick. The best experimental evidence for the solid film theory was provided by the National Bureau of Standards which undertook a comprehensive study of the passivating process (61). Ellipsometric measurements of "film-free" iron surfaces and of film growth in inorganic passivating solutions confirm the oxide theory of passivity. Results from recent studies suggest that the film consists primarily of an outside layer of Fe₂O₃ and a small quantity of Fe₃O₄ at the electrode film interface. If Vetter's views on high-field ion conduction are correct the discrepancies which exist between the reversible passivation potential reported by Flade and the potential expected from the formation of such a duplex film can be readily explained.

The influence of pH on the passivity of iron in hydrogen-saturated solutions of sulfuric acid is shown in the polarization diagrams presented in Figure 44. In addition, values of the passive current density are tabulated on
page 217. It is obvious that a direct correlation between the hydrogen ion concentration and the magnitude of the passive current density, at least in dilute solutions of sulfuric acid, does not exist.

**Chromium**

Unlike iron, the hydrogen ion concentration is the deciding factor for the onset of passivation of chromium. This effect is reflected in the anodic polarization diagrams of chromium in sulfuric acid. The presence of the cathodic dip and the change in magnitude of the passive current density (Table 20) as a function of pH are inherent in the following mechanism proposed by Roberts and Shutt (49).

Since chromium atoms carrying adsorbed oxygen atoms are no longer available for ionization as chromous salts, the metal is further oxidized by the discharge of anions upon them. The discharge process, responsible for the cathodic dip in the polarization curve, is favored in solutions of low acidity. As a result of this process the valency of the chromium atoms is increased until they become detached from the lattice and pass into solution as chromate ions. These strongly oxidizing anions undoubtedly remain in the vicinity of the anode due to electrical migration. Chromium atoms exposed on the surface of the electrode are subsequently oxidized, either by hydroxyl or by chromate
ions, and are converted to an intermediate oxide such as CrCrO$_4$. The current density at this point increases as the potential is moved in the positive direction. Roberts and Shutt (49) concluded that "in the comparatively alkaline diffusion layer, such substances will be quite insoluble and will form, on the anode, a loose and eventually a thick layer of oxide, or hydrate oxide, whose exact composition may vary with the precise conditions of its formation."

Once the adsorbed film of oxide is formed very low currents should suffice to build the macroscopic layer.

**Nickel**

The phenomenon leading to the onset of passivation of nickel in hydrogen saturated sulfuric acid has been the subject of much controversy. Since the exact interpretation of the process is not known, only a brief description of the mechanism can be formulated from the reported literature.

In the active region of the polarization curve the dissolution of nickel atoms leads to the formation of a basic nickel sulfate. Beyond this point, nickel atoms are no longer able to pass into solution and the discharge of hydroxyl ions becomes the predominant reaction (51).

The concentration of hydroxyl ions in the vicinity of the electrode increases until an adsorbed layer of NiOH$^+$
is formed (52). When the nickel is polarized to a certain potential described by the relation

$$E = 0.723 - 0.1475pH - 0.0885 \log [\text{NiOH}^+] \text{ (volts)}$$  \hspace{1cm} (179)

a higher valency oxide is formed. The passivation current density is found to be dependent upon the hydrogen ion concentration of the solution according to the expression

$$\log i_0 = -1.10 - 0.83 \text{ pH (amp./cm}^2\text{)}$$  \hspace{1cm} (180)

The exact composition of the oxide film depends on the conditions under which it is formed and on the oxygen content of the environment to which it is exposed. Sato and Okamoto (62) concluded that the oxide is $\text{Ni}_3\text{O}_4$, whereas Prazak and Prazak (63) reported it to be $\text{Ni}_2\text{O}_3$ or a composite of $\text{NiO}$ and $\text{NiO}_2$.

The effect of pH on the magnitude of the passive current density is reflected in the polarization curves shown in Figure 46 and in the values tabulated on page 217. The data indicate that the stability of the passive film decreases with increasing acidity of the solution in agreement with the results reported by Economy, Speiser, Beck, and Fontana (55).

**Iron-chromium-nickel alloys**

The passive state of metals is further complicated by the introduction of alloying elements. In some cases the
passive film may consist of a composite of mixed oxides or, in other cases, it may contain impurity atoms or other imperfections. Furthermore, each oxidation state of the imposing alloying cases, it may contain impurity atoms or other imperfections. Furthermore, each oxidation state of the imposing alloying element may be stable only in a particular potential range. When this occurs, the composition of the film may change continually from one potential or environment to another. Small changes in the composition of the oxide may substantially alter its electrical and chemical properties.

According to Schwenk and Rohmel (64) there are essentially three different types of films which can form on electrodes in aqueous solutions. They are—

1. Nonconducting,
2. Ion-conducting, and

Fortunately, the passive layer on chromium and/or nickel containing steels is similar to that formed on iron and belongs in the last group.

An effective composition of the passive layer on stainless steel which satisfies all experimental requirements is so far unknown. It is thought, however, that the film is composed of trioxides of iron, chromium, and nickel, each existing with their own crystalline lattice or combined in
the form of a spinel. These oxides are highly resistant and less soluble than oxides of lower valency (63). Even more complex ratios can be expected in mixed oxides originating on highly alloyed materials.

Stability of the passive state is determined by the relative ease in which the trivalent components are reduced to the more soluble bivalent oxides and by the rate at which the film is replenished during the passage of current. This rate is expressed by the magnitude of the current density in the passive state. The latter depends on the corrosiveness of the environment.

The beneficial effect of chromium on the corrosion resistance of iron is inherent in its more active electrochemical nature. It was previously noted that chromium favors the onset of passivation by reducing the critical current density and displacing the passivation potential in the negative direction. The values of the passive current density presented in Table 18 show that chromium also lowers the corrosion current in the passive state. This effect is lessened when the nickel content is raised, since nickel tends to lower the stability of the passive film in dilute solutions of sulfuric acid. Results from this study appear to confirm the observations made by Cihal and Prazak (31) that the corrosion resistance of chromium-nickel steels is
not due to their structure, but rather to their chemical composition.

The corrosion resistance of stainless steel in the passive state can be further improved by the judicious choice of additional alloying elements, such as phosphorous, oxygen, silicon, copper, molybdenum, sulfur, and nitrogen. These elements are observed to decrease the passive current density under the given experimental conditions. Manganese has little effect on the magnitude of the corrosion current, whereas additions of platinum and carbon apparently decrease the stability of the passive film. The effect of fourth-component additions is difficult to analyze, for example some induce self-passivity despite the fact that they increase the corrosion current in the passive state. Others are observed to shorten or to lengthen the potential range over which passivity is found. Therefore, the evaluation of each element is based solely on the manner in which it influences the passive current density. Obviously, this is not the only criterion on which the effectiveness of alloying elements is judged. It is apparent that other properties must be considered.

F. Transpassive behavior

The upper boundary marking the stability of the passive layer is the transpassive potential. At high
potentials the measured current increases and the protective properties of the film are destroyed. The value of the transpassive potential and the rate of the corresponding oxidation reaction depends on the acidity of the electrolyte and on the composition of the anode. In some cases, the components of the passive film on the electrode are oxidized to a much higher soluble form and in other cases the current rise is associated with oxygen evolution. Prazak (29) concluded that corrosion in the transpassive region apparently does not take place often because such strongly oxidizing environments, which would take the material into such a high positive potential range, are relatively scarce.

When certain metals are subjected to a potential more noble than the equilibrium oxygen electrode potential, oxygen evolution becomes one of the primary oxidation reactions. According to Stern (65), metal dissolution still occurs and generally at a rate higher than that which exists in the passive range. This behavior is exhibited by iron in dilute solutions of sulfuric acid at ambient temperatures. The shift in the transpassive potential in the negative direction with increasing pH is a consequence of the change in potential of the reversible oxygen electrode,

\[ E_{O_2} = 1.23 + \frac{RT}{4F} \log (a_{H^+})^4 (p_{O_2}) \]  (181)
which at $25^\circ C$ and one atmosphere of oxygen pressure reduces to

$$E_{o_2} = 1.23 - 0.05915 \text{ pH}$$  \hspace{1cm} (182)

Under similar conditions, the pH-potential relationship indicated by this equation is also valid for other metals. Not all metals, however, exhibit oxygen evolution. The rise in current density, for example, observed for pure chromium in sulfuric acid is due to the formation and accumulation of $\text{CrO}_3$ within the pores of the passive film. The transpassive behavior is described by a Tafel slope of approximately $0.040$ volts which is displaced in the positive direction with increasing acid concentration (66).

The transpassive potential of nickel, on the other hand, is indicative of still another oxidation process. If the concentration of $\text{NiO}_2$ (which is highly soluble in sulfuric acid) in the passive nickel layer is increased, the rise in current density can be attributed to anodic dissolution instead of oxygen evolution. Myers, Beck, and Fontana (67) observed that the Tafel line which describes the transpassive behavior of pure nickel in this potential range is shifted in the negative direction with increasing acid concentration, in agreement with results from this investigation.

At still higher potentials nickel exhibits a deflection in the transpassive region. This dip is ascribed to the
adsorption of oxygen at potentials prior to the evolution of gaseous oxygen and is commonly referred to as secondary passivity. Since the state of passivity is incomplete the current density decreases only slightly below its value at the transpassivity maximum. It is apparent from the polarization diagrams (refer to Figure 46) that the tendency to exhibit secondary passivity is lessened in solutions of low acidity. Secondary passivity is insignificant from a practical point of view since the potential necessary to reach this state is exceedingly high, as is the rate of metal dissolution. Oxygen evolution takes place above this potential range and is represented by a Tafel slope of about 0.95 volts which is found to be independent of pH (67).

The passive layer on chromium-nickel steels is disrupted in a manner similar to that of its components. At the transpassive potential the trivalent metal oxides become unstable and pass into solution as soluble ions. The dissolution reaction, at least in chromium-containing steels, is apparently controlled by the formation of chromate ions which are extremely soluble in aqueous environments. The effect of chromium and other alloying elements on the corrosion current of iron-base alloys in the regions of transpassivity and secondary passivity is clearly indicated in the corresponding polarization diagrams. Since these diagrams were obtained at a scan rate of approximately
100 millivolts per minute the magnitude of the characteristic points may differ from those obtained under equilibrium conditions. A predominate trend in the transpassive region as a result of alloying, can, however, be observed.

Chromium additions of 10 and 20 per cent to pure iron shift the transpassive potential in the negative direction and increase the rate of corrosion in the transpassive region considerably. Cihal and Frazak (31) report that when the chromium content is increased to 30 per cent the formation of soluble chromate ions supersedes the evolution of oxygen and the alloy behaves like pure chromium. Nickel has little effect on the transpassive potential of iron-chromium alloys but it does increase the corrosion rate slightly at high potentials.

When nickel alone is added to iron, secondary passivity does not appear until the nickel content exceeds 10 per cent of the total composition. At higher nickel contents the corrosion current is increased in both the transpassive and secondary passive regions.

It is interesting to note that all the fourth-component additions displace the transpassive potential of Alloy 54 in the positive direction. However, little effect, if any, on the magnitude of the corrosion current in either the transpassive or secondary passive regions can be detected. Of all the elements studied, only carbon and manganese
produced a noticeable deflection in the polarization curve at potentials beyond the transpassive potential. Petit and Epelboin (68) observed that austenitic Type 18-8 steels show no secondary passivity if their carbon contents are sufficiently low in apparent agreement with the above results.

For reasons of comparison the polarization curve of a commercial grade of stainless steel which contains many of the fourth-component additions is shown in Figure 43.
VI RECOMMENDATIONS FOR ADDITIONAL WORK

This investigation is part of a program sponsored by the Atomic Energy Commission to establish details of a mechanism for the stress corrosion cracking of iron-chromium-nickel alloys in aqueous environments. It is anticipated that a study of the polarization behavior of these alloys will enhance our knowledge of the inherent electrochemical processes. Electrochemical observations will be correlated with occurrences of stress corrosion cracking in a specially designed autoclave system.

In the initial stages of the program numerous experimental techniques were evaluated to find the most fruitful approach to the study of the stress corrosion cracking mechanism. Studies of the electrochemical behavior of high-purity iron-rich iron-chromium-nickel alloys in hydrogen-saturated solutions of sulfuric acid were conducted. Composition, microstructure, temperature, and solution pH were found to have significant affects on polarization characteristics.

In view of the above, the following recommendations for additional work are suggested:

1. Extend the present investigation to include the complete iron-chromium-nickel alloy system.
2. Compute the shape of anodic polarization diagrams for binary and ternary alloys from curves of their components.

3. Examine, in detail, the dissolution kinetics of specially prepared alloys, particularly the dissolution ratio of their constituents. Use of irradiated specimens is suggested.

4. Determine the effect of stress on the anodic polarization behavior of these alloys in sulfuric acid, utilizing the electrode mount described by Greene, Acello, and Greif (69) for electrochemical studies of stressed metal specimens.

5. Conduct an extensive investigation in aqueous chloride solutions in which stress corrosion cracking occurs. In these environments the effect of stress, temperature, and alloy composition on the breakdown potential of passive films can be studied advantageously. In addition, an investigation of the effect of chloride concentration and oxygen content of the chloride media on pitting corrosion and on the initiation of stress corrosion cracking sites should make an important contribution to mechanistic studies.
BIBLIOGRAPHY


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33. Engineering Department of Industrial Instruments, Inc., Industrial Instruments, Inc., 89 Commerce Road, Cedar Grove, New Jersey.


46. Flade, F. "Beiträge zur Kenntnis der Passivität." Zeitschrift für physikalische Chemie, 76 (1911), 513-559.


57. HOAR, T. P., and HAVENHAND, D. "Factors Influencing the Rate of Attack of Mild Steels by Typical Weak Acid. Jnl. Iron & Steel Inst., 133 (1936), 239P.


